

## RESEARCH REPORT

(to protect the scientific priority, only published results are presented here)

January 2012 – December 2016

### New Organometallic Compounds of Heavy Group 15 Metals (Antimony, Bismuth) -- Potential Use in Catalysis

PN-II-ID-PCE-2011-3-0933

#### Scientific objectives for phase 2012

In 2012 was accomplished an exhaustive literature search covering the topic intended to be developed within the project, an activity which resulted in a review published in a high ranked international journal (submitted for publication in 2012, published in 2013: C. I. Raț, C. Silvestru, H. J. Breunig, *Coord. Chem. Rev.*, **2013**, 257, 818-879; DOI: 10.1016/j.ccr.2012.07.026). In addition the following exploratory studies were carried out to obtain the target compounds:

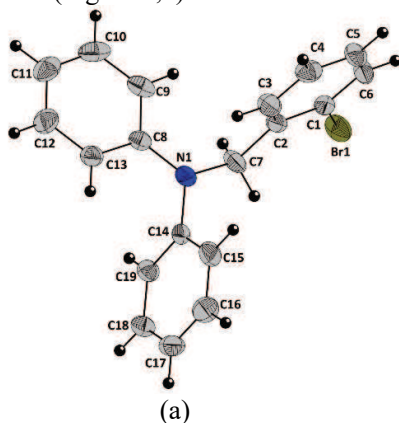
#### Chiral organometallic compounds (Sb, Bi) with organic ligand bearing one or two pendant arms

For the compounds intended to be investigated within this project the chirality can arise due to different reasons, e.g. (i) the organic ligand has a chiral carbon atom or heteroatom; (ii) the metal atom is chiral due to the presence of three different substituents attached to it; (iii) induced chirality at the metal centre through intramolecular coordination.

New ligands with one or two pendant arms were prepared. For some of the precursors with one pendant arm new synthetic procedures were established leading to good yields of the desired compounds. Using such ligands, as [2-(Ph<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>Br (1) (Figure 1,a), 2-[Mes(Me)NCH<sub>2</sub>]C<sub>6</sub>H<sub>4</sub>Br (2) and related derivatives, new organoantimony(III) compounds were prepared:

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Both the organic precursors and the organometallic species were characterized by NMR spectroscopy and mass spectrometry. For compound 9 the molecular structure was established by single crystal X-ray diffraction (Figure 1,b).



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Figure 1. Molecular structure of compounds (a) 2-(Ph<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>Br (1), and (b)

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The studies concerning the organoantimony(III) compounds with ligands of type 2-(2',6'-i-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>N=CH)C<sub>6</sub>H<sub>4</sub> and 2-(2',4',6'-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>N=CH)C<sub>6</sub>H<sub>4</sub>, in part accomplished within the previous research project (PN-II-ID-2052/2009), were finalized and the results were published in an article (submitted for publication in 2012, published in 2013: A. M. Preda, C. I. Raț, C. Silvestru, H. J. Breunig, H. Lang, T. Rüffer and M. Mehring, *Dalton Trans.*, **2013**, 42, 1144-1158; DOI: 10.1039/C2DT32494F). It should be mentioned here that this paper was selected to illustrate the cover of the corresponding issue of the prestigious journal *Dalton Transactions*. The imino organic ligands were also used to obtain new organobismuth(III) compounds. The chlorides

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in air.

were isolated as yellow crystalline powders, stable

New chiral halides of the type

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respectively [2-{(2',6'-i-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)N=CH}C<sub>6</sub>H<sub>4</sub>]PhSbCl (16), were isolated as air stable, crystalline white or yellow compounds. The compounds were characterized by elemental analysis, NMR and IR spectroscopy, mass spectrometry.

For several organoantimony(III) and –bismuth(III) species, *e.g.* **11** (Figure 2,a) and **16** (Figure 2,b), the crystal and molecular structure was established by single-crystal X-ray diffraction.

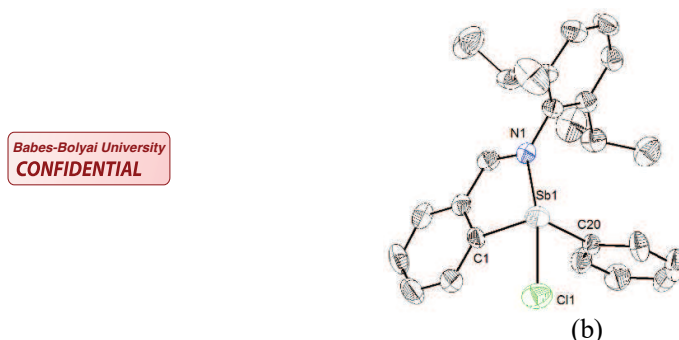


Figure 2. Molecular structures of isomers (a) , și (b) ( $C_{sb}$ )-16.

### Oxides and hydroxides/alkoxides, as well as ionic organometallic compounds (Sb, Bi)

Chiral oxides of the type  $(RR'M)_2O$  and  $(RMO)_2$  were prepared using organometallic halides described above. Thus, the oxide (17) was obtained by reacting the chloride **12** with KOH, in a mixture of solvents, *i.e.* water /  $CH_2Cl_2$ . This oxide was isolated as a white, crystalline solid. All the oxides prepared were spectroscopically characterized.

The synthesis of organometallic hydroxides and alkoxides appeared to be much more difficult, in most cases only oxides being obtained following elimination of water or ethers. The studies concerning the stabilization of such species were continued in next phases as result of the serendipitous isolation of the ionic species (18). The cation of this compound is chiral and the crystal contains a racemic mixture [ $(C_{sb})$  and  $(A_{sb})$  isomers] (Figure 3,a).

Preliminary evaluations were performed to establish the ability of some organobismuth(III) and organoantimony(III) oxides to react with  $CO_2$  or to catalyze reactions to obtain polycarbonates and/or cyclic organic carbonates from epoxides and  $CO_2$ .

The monochlorides  $[2-(Me_2NCH_2)C_6H_4]_2SbCl$  and **16** react with  $Ag[SbF_6]$  or  $Tl[PF_6]$  to give ionic species with diorganoantimony(III) cations. Treatment of the ionic compound  $[(2-\{(2',6'-Pr'_2C_6H_3)N=CH\}C_6H_4)PhSb][PF_6]$  (**20**) with  $[Bu_4N]F \cdot 3H_2O$  gave the fluoride  $[2-\{(2',6'-Pr'_2C_6H_3)N=CH\}C_6H_4]PhSbF$  (**21**). The solution behaviour of the new ionic compounds **18** și **11** and of the fluoride **21** was investigated by multinuclear ( $^1H$ ,  $^{13}C$  și  $^{19}F$ ) NMR spectroscopy and the molecular structures of **18** și **21** were established by single-crystal X-ray diffraction (Figure 3).

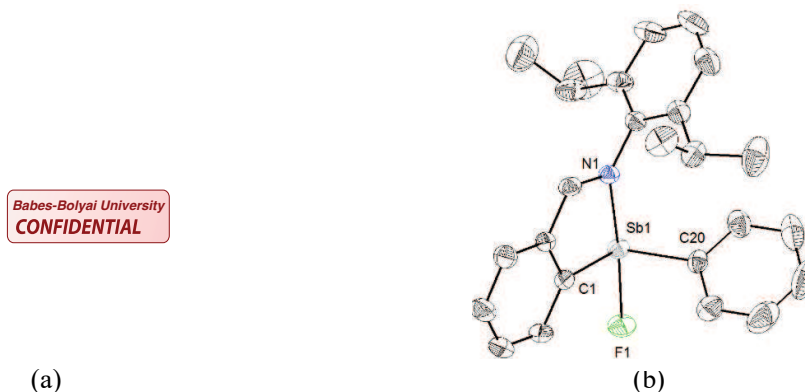


Figure 3. Structures of (a) ionic compound ( $A_{sb}$ )-18, and (b) fluoride ( $C_{sb}$ )-21.

Within a collaboration with the research group of Prof. Ulrich Körtz (Jacobs University, Bremen, Germany) organoantimony(III) fragments –  $PhSb(III)$  and  $[2-(Me_2NCH_2)C_6H_4]Sb$  – were successfully incorporated in discrete heteropolytungstate anions, the results obtained being published in a joint paper (M. Barsukova-Stuckart, L. F. Piedra-Garza, B. Gautam, G. Alfaro-Espinoza, N. V. Izarova, A. Banerjee, B. Bassil, M. Ullrich, H. J. Breunig, C. Silvestru and Ulrich Körtz, *Inorg. Chem.*, **2012**, *51*, 12015-12022; DOI: 10.1021/ic301892s).

Due to difficulties concerning the preparation of new hypervalent  $R_2Bi-BiR_2$  species by reduction of the organometallic halides obtained during this phase of the project, this target was postponed for future phases of the project.

### Complecși cu metale tranziționale

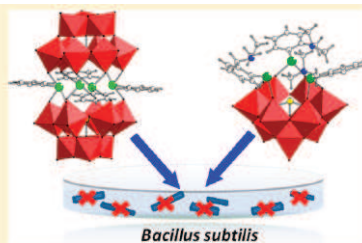
Preliminary studies to obtain transition metal complexes (Ni, Pd) with chiral hypervalent compounds of the type  $RSbPh_2$  were performed. Reactions between  $[2-(Ph_2NCH_2)C_6H_4]SbPh_2$  (**5**) or  $[2-\{Mes(Me)NCH_2\}C_6H_4]SbPh_2$  (**9**) and

(cod)PdCl<sub>2</sub> (cod = 1,5-cyclooctadiene) were carried out in THF, at room temperature. The work-up of the reaction mixtures did not yet produced pure complexes.

### Publications appeared in 2012

1. Synthesis and characterization of organoantimony(III)-containing heteropolytungstates, M. Barsukova-Stuckart, L. F. Piedra-Garza, B. Gautam, G. Alfaro-Espinoza, N. V. Izarova, A. Banerjee, B. Bassil, M. Ullrich, H. J. Breunig, C. Silvestru and Ulrich Kortz, *Inorg. Chem.*, **2012**, *51*, 12015-12022.  
DOI: 10.1021/ic301892s

**ABSTRACT:** Three discrete organoantimony(III)-containing heteropolytungstates [(PhSb<sup>III</sup>)<sub>4</sub>(A-α-Ge<sup>IV</sup>W<sub>9</sub>O<sub>34</sub>)<sub>2</sub>]<sup>12-</sup> (1), [(PhSb<sup>III</sup>)<sub>4</sub>(A-α-P<sup>V</sup>W<sub>9</sub>O<sub>34</sub>)<sub>2</sub>]<sup>10-</sup> (2), and [{2-(Me<sub>2</sub>NCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)Sb<sup>III</sup>}]<sub>3</sub>(B-α-As<sup>III</sup>W<sub>9</sub>O<sub>33</sub>)<sup>3-</sup> (3) have been synthesized in one-pot reactions in aqueous medium using the appropriate lacunary heteropolyanion precursor and organoantimony(III) source. Polyanions 1–3 were isolated as hydrated salts, (NH<sub>4</sub>)<sub>12</sub>[(PhSb<sup>III</sup>)<sub>4</sub>(A-α-Ge<sup>IV</sup>W<sub>9</sub>O<sub>34</sub>)<sub>2</sub>].20H<sub>2</sub>O (1a), Rb<sub>9</sub>Na[(PhSb<sup>III</sup>)<sub>4</sub>(A-α-P<sup>V</sup>W<sub>9</sub>O<sub>34</sub>)<sub>2</sub>].20H<sub>2</sub>O (2a), and Rb<sub>3</sub>[{2-(Me<sub>2</sub>NCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)Sb<sup>III</sup>}]<sub>3</sub>(B-α-As<sup>III</sup>W<sub>9</sub>O<sub>33</sub>).7H<sub>2</sub>O (3a). The compounds 1a–3a were fully characterized in the solid state using infrared (IR) spectroscopy, single-crystal XRD, and thermogravimetric and elemental analyses. The stability of 1–3 in aqueous solution was confirmed by multinuclear NMR (<sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P, and <sup>183</sup>W) spectroscopy. Preliminary studies on the biological activity of 1–3 showed that all three compounds might act as potent antimicrobial agents.



### Contributions to national and international conferences

- C1. Chiral hypervalent organoantimony(III) cations, A. M. Preda, H. Lang, T. Rüffer, M. Mehring and C. Silvestru, at *The XXV International Conference on Organometallic Chemistry (ICOMC)*, Lisbon (Portugal), Sept. 2-7, **2012**.

### Scientific objectives for phase 2013

#### Chiral organometallic compounds (Sb, Bi) with organic ligand bearing one or two pendant arms

Several new organic ligands with one pendant arm, *e.g.* 2-(Ph<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>Br (**1**) or 2-[Mes(Me)NCH<sub>2</sub>]C<sub>6</sub>H<sub>4</sub>Br (**2**), prepared during the previous phase, were used for the synthesis of chiral organoantimony(III) and organobismuth(III) species, *e.g.*

All these compounds were investigated by NMR spectroscopy and mass spectrometry, and the molecular structure of **25** was established single-crystal X-ray diffraction (Figure 4,a).

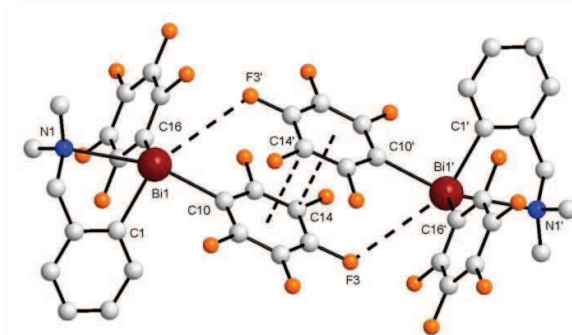
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Several attempts to use the proligand 2-[Mes(Me)NCH<sub>2</sub>]C<sub>6</sub>H<sub>4</sub>Br (**2**) in order to improve the yield of the synthesis of compound **(7)**, reported in the previous phase, have failed. In addition a new chiral compound (**29**) was isolated. This compound is air and moisture stable and was characterized by NMR spectroscopy, mass spectrometry and single-crystal X-ray diffraction (Figure 4,b). The molecules of both dihalide **25** and unexpected compound **29** contain a nitrogen atom strongly coordinated intramolecularly to antimony, thus resulting in hypervalent species. These results will be the subject of a paper still in preparation.

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Studies on chiral organobismuth(III) containing  $C_6F_5$  groups on the metal centre were continued. Studies on chiral organobismuth(III) containing  $C_6F_5$  groups on the metal centre were continued. [2-( $Me_2NCH_2$ ) $C_6H_4$ ]( $C_6F_5$ ) $_2$ Bi (**30**) was obtained by reacting [2-( $Me_2NCH_2$ ) $C_6H_4$ ]BiCl $_2$  and  $C_6F_5$ MgBr (method A) or  $C_6F_5$ Li (method B), in 1:2 molar ratio. Other chiral bromides [2-( $Me_2NCH_2$ ) $C_6H_4$ ](Ar)BiBr [Ar =  $C_6F_5$  (**31**), Mes (**32**)] and [2-( $Me_2NCH_2$ ) $C_6H_4$ ](Ph)BiBr (**33**) were also obtained.

The compounds were isolated as crystalline, colorless solids, soluble in organic solvents. The compounds **32** and **33** are stable in air, while the derivatives with  $C_6F_5$  groups on bismuth, **30** și **31**, decomposed in solution in few hours in solution. All four compounds were characterized by NMR spectroscopy in solution and by mass spectrometry and their molecular structure was established single-crystal X-ray diffraction. In the crystal there were evidenced dimeric associations (e.g. in **30**, Figure 5) or 3D architectures based on Bi $\cdots$ halogen, H $\cdots$ halogen, H- $\pi$  or  $\pi$ - $\pi$  intermolecular interactions.



**Figure 5.** Dimer association through Bi $\cdots$ F and  $\pi$ - $\pi$  interactions in the crystal of compound [2-( $Me_2NCH_2$ ) $C_6H_4$ ]( $C_6F_5$ ) $_2$ Bi (**30**).

The results obtained in the study of these chiral derivatives with  $C_6F_5$  groups attached to bismuth and of the related species **32** are the subject of an article published in 2016 (M. Olaru, M. Nema, A. Soran, H. J. Breunig and C. Silvestru, *Dalton Trans.*, **2016**, 45, 9419-9428; DOI: 10.1039/C5DT05074J).

### Organoantimony(III) ionic species and fluorides

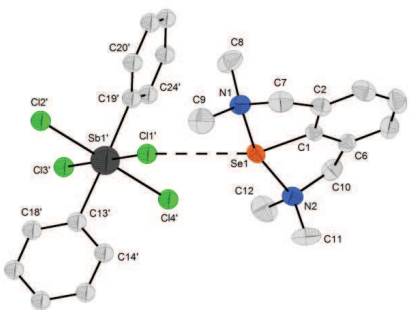
The studies on the synthesis of diorganoantimony(III) cations and their use to prepare diorganoantimony(III) fluorides were continued and developed to get new chiral species stabilized using ligands with pendant arms, e.g. 2-[2',6'- $i$ -Pr $_2$  $C_6H_3$ N=CH] $C_6H_4$  and 2-[2',4',6'- $Me_3$  $C_6H_2$ N=CH] $C_6H_4$ . In addition to the researches done in 2012 [ionic compounds

(**18**) and [(2-{(2',6'- $i$ -Pr $_2$  $C_6H_3$ )N=CH} $C_6H_4$ )PhSb][PF $_6$ ] (**20**), and the fluoride [2-{(2',6'- $i$ -Pr $_2$  $C_6H_3$ )N=CH} $C_6H_4$ ]PhSbF (**21**)], the preparation of new organoantimony(III) cations stabilized by using ligands with pendant arms was performed: [R $_2$ Sb] $^+$ [PF $_6$ ] $^-$  (**34**) (R = 2-[2',6'- $i$ -Pr $_2$  $C_6H_3$ )N=CH] $C_6H_4$ ) and [R' $_2$ Sb] $^+$ [PF $_6$ ] $^-$  (**35**) (R' = 2-[2',4',6'- $Me_3$  $C_6H_2$ )N=CH] $C_6H_4$ ). These compounds were obtained by treating the corresponding bromides with Tl[PF $_6$ ], in THF, at room temperature. Similarly, the reaction between [2-( $Me_2NCH_2$ ) $C_6H_4$ ](Ph)SbCl and Ag[SbF $_6$ ] gave the ionic derivative [{2-( $Me_2NCH_2$ ) $C_6H_4$ ](Ph)Sb(thf)] $^+$ [SbF $_6$ ] $^-$  (**36**). Treatment of these ionic compounds with [Bu $_4$ N]F $\cdot$ 3H $_2$ O led to the formation of chiral organoantimony(III) fluorides: R $_2$ SbF (**37**), [2-( $Me_2NCH_2$ ) $C_6H_4$ ] $_2$ SbF (**38**) and [2-( $Me_2NCH_2$ ) $C_6H_4$ ](Ph)SbF (**39**). It was established a **general, unique procedure for the preparation of diorganoantimony(III) fluorides**, compounds which cannot be prepared using common methods of fluorination.

The solution behaviour of these new ionic compounds **18**, **20**, **34**, **35** și **36**, as well as of the corresponding fluorides **21**, **37-39**, was investigated by NMR ( $^1$ H,  $^{13}$ C și  $^{19}$ F) spectroscopy at room temperature and for compounds **20**, **34**, **35**, **37**, **38** și **39** the molecular structure was established single-crystal X-ray diffraction. The results obtained in the study of these diorganoantimony(III) derivatives are the subject of an article published in 2015 (A. M. Preda, C. I. Raț, C. Silvestru, H. Lang, T. Rüffer and M. Mehring, *RSC Advances*, **2015**, 5, 99832-99840; DOI: 10.1039/c5ra21788a).

Another strategy to obtain ionic organopnictogen species was based on the transfer of the chlorine atom from [{2,6-( $Me_2NCH_2$ ) $_2$  $C_6H_3$ }Se] $^+$ Cl $^-$  to the metal atom of organometallic chlorides of the type R' $_2$ MCl $_n$ .

Several new compounds with organobismuth(III), -antimony(III) and antimony(V) anions were prepared: [{2,6-( $Me_2NCH_2$ ) $_2$  $C_6H_3$ }Se] $^+$ [R' $_2$ MCl $_{n+1}$ ] $^-$  [R' = 2-( $Me_2NCH_2$ ) $C_6H_4$ ,  $n$  = 1, M = Sb (**40**), Bi (**41**); R' = Ph, M = Sb,  $n$  = 1 (**42**) or  $n$  = 3 (**43**)]. The compounds were investigated in solution by multinuclear NMR spectroscopy ( $^1$ H,  $^{13}$ C,  $^{77}$ Se, 2D experiments). The ionic nature of these compounds containing diorganoantimonate anions was confirmed by conductometric studies and by the solid state structure determination by single-crystal X-ray diffraction for [{2,6-( $Me_2NCH_2$ ) $_2$  $C_6H_3$ }Se] $^+$ [Ph $_2$ SbCl $_4$ ] $^-$  (**43**) (Figure 6). The results were published in an article which also includes theoretical calculations on these ionic species published in 2014 (A. Pop, A. Silvestru, E. J. Juárez-Pérez, M. Arca, V. Lippolis and C. Silvestru, *Dalton Trans.*, **2014**, 43, 2221-2233; DOI: 10.1039/C3DT52886C).



**Figure 6.** The structure of the ionic compound  $[2,6-(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3\}\text{Se}]^+[\text{Ph}_2\text{SbCl}_4]^-$  (**43**).

#### Organometallic (Sb, Bi) oxides and hydroxides/alkoxides

Studies were performed on the synthesis and characterization of new organoantimony(III) compounds containing the ligand  $2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4$ , which might exhibit potential uses for the activation of small molecules. For this purpose the pnictogen/boron dinuclear species seem to be very promising since they have in the same molecule both Lewis acid and Lewis base centers. The oxide  $(\text{RSbO})_3$  was reacted with  $\text{PhP}(\text{O})(\text{OH})_2$ ,  $\text{F}_3\text{CC}(\text{O})\text{OH}$ ,  $\text{MesB}(\text{OH})_2$  and  $\text{Me}_5\text{C}_6\text{B}(\text{OH})_2$  to produce new compounds (**44–48**) (Scheme 1), which were characterized through spectroscopic methods.

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The molecular structure of **46** was established by single-crystal X-ray diffraction on crystals grown by slow diffusion of petroleum ether into a chloroform solution of the compound (Figure 7).

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**Figure 7.** Molecular structure of compound

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(**46**).



### Catalytic studies

The catalytic activity of some of the new chiral, hypervalent ionic organoantimony(III) compounds was investigated and studies on the efficiency on "one-pot" diastereoselective Mannich reactions were performed. This reaction is a useful way to build new C-C bonds. For the system of reagents used (benzaldehyde, aniline and cyclohexanone) it was observed that the reaction is fast and efficient, with very good yields, depending on the reaction solvent. The *anti/syn* ratio in the reaction mixture was established by NMR spectroscopy.

It was established that the catalytic activity of the screened ionic species is higher than that of a neutral diorganoantimony(III) bromide or  $SbCl_3$ , in ethanol or acetonitrile.

Preliminary results were reported within a scientific conference on catalysis (C3 on the list of contributions to national and international conferences); the studies will be continued and finalized in a publication during the next phases of the project.

### Transition metal complexes

The studies on the synthesis and characterization of new palladium complexes with chiral, hypervalent organoantimony(III) ligands of the type  $[2-(Me_2NCH_2)C_6H_4]PhSbCl$  and  $[2-(Me_2NCH_2)C_6H_4]Mes_2Sb$  were continued. The stable species  $[(Me_2NHCH_2)C_6H_5][\{2-(Me_2NCH_2)C_6H_4\}(Ph)(Cl)SbPdCl_3]$  (50) and *cis*- $[PdCl_2\{2-(Me_2NCH_2)C_6H_4\}Mes_2Sb]$  (51) were isolated and characterized in solution and solid state. Theoretical calculation at DFT level were carried out to get information on the nature of the coordinative bonds in these complexes. The results were published in an article published in 2014 (D. Copolovici, F. Isaia, H. J. Breunig, C. I. Raţ and C. Silvestru, *RSC Advances*, **2014**, 4, 26569-26576; DOI: 10.1039/c4ra03482a).

### Publications appeared in 2013

#### 1. Hypervalent organoantimony and -bismuth compounds with pendant arm ligands,

C. I. Raţ, C. Silvestru and H. J. Breunig,  
*Coord. Chem. Rev.*, **2013**, 257, 818-879.

DOI: 10.1016/j.ccr.2012.07.026

#### ABSTRACT

Recent developments in chemistry of hypervalent organoantimony and -bismuth complexes with bidentate (C,E)- and tridentate (E,C,E)- and (C,E,C)-ligands are reviewed. The ligands are bonded to the antimony or bismuth atoms through carbon atoms and through intramolecular coordination with dative bonds from nitrogen, oxygen or sulfur atoms. Syntheses, structures including chirality aspects, reactions, fluxional behavior, biological aspects and applications in the field of catalysis and organic syntheses are considered in this review.

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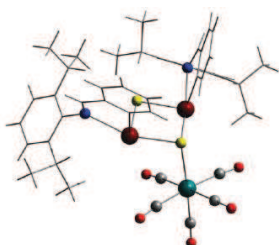
#### 2. Organoantimony(III) compounds containing (imino)aryl ligands of the type $2-(RN=CH)C_6H_4$ ( $R = 2',4',6'-Me_3C_6H_2$ , $2',6'-iPr_2C_6H_3$ ): bromides and chalcogenides,

A. M. Preda, C. I. Raţ, C. Silvestru, H. J. Breunig, H. Lang, T. Rüffer and M. Mehring,

*Dalton Trans.*, **2013**, 42, 1144-1158.

DOI: 10.1039/C2DT32494F

The reaction of  $2-(RN=CH)C_6H_4MgBr$  [ $R = 2',4',6'-Me_3C_6H_2$  ( $R^1$ ),  $2',6'-iPr_2C_6H_3$  ( $R^2$ )] [prepared from  $2-(R^1N=CH)C_6H_4Br$  (1) or  $2-(R^2N=CH)C_6H_4Br$  (2) and Mg] with  $SbCl_3$  in a 2 : 1 and 1 : 1 molar ratio followed by treatment with an aqueous KBr solution gave  $[2-(R^1N=CH)C_6H_4]_2SbBr$  (3) and  $[2-(R^2N=CH)C_6H_4]_2SbBr$  (4) as well as  $[2-(R^1N=CH)C_6H_4]SbBr_2$  (6) and  $[2-(R^2N=CH)C_6H_4]SbBr_2$  (7). Treatment of 4 with  $Na_2S \cdot 9H_2O$  provided the dinuclear  $[[2-(R^2N=CH)C_6H_4]_2Sb]_2S$  (5). Heterocyclic species, i.e. the oxide *cyclo*- $[[2-(R^2N=CH)C_6H_4]SbO]_3$  (8) and the sulfides *cyclo*- $[[2-(R^1N=CH)C_6H_4]SbS]_2$  (9) and *cyclo*- $[[2-(R^2N=CH)C_6H_4]SbS]_2$  (10), were obtained by reacting dibromides 6 and 7 with KOH and  $Na_2S \cdot 9H_2O$ , respectively, in a water-toluene solvent mixture. The sulfide 10 reacted with  $[W(CO)_5(thf)]$  to yield the heterometallic complex *cyclo*- $[[2-(R^2N=CH)C_6H_4]SbS]_2[W(CO)_5]$  (11). The compounds were characterised by multinuclear NMR spectroscopy in solution, mass spectrometry and IR spectroscopy in the solid state. The molecular structures of 4, 5, 6- $CHCl_3$ , 7, 9- $CH_2Cl_2$ , 10 and 11-0.25 $CH_3OH$  were established by single-crystal X-ray diffraction. Theoretical calculations using DFT methods were carried out on bromide 7 and the geometrical isomers of its dimer association as well as the geometrical isomers of sulfide 10 and its monomer.



### Contributions to national and international conferences

- C1. Organometallic compounds - unusual species stabilized through intramolecular coordination, C. Silvestru, at *A 9-a Sesiune de Comunicări Științifice Studentești*, Universitatea București, București, May 17, **2013** (invited opening plenary lecture).
- C2. The use of hypervalent organoantimony(III) cations as catalysts in the Mannich reactions, A. M. Preda, C. Silvestru, at *The international Symposium of The Romanian Catalysis Society, (RomCat2013)*, Cluj-Napoca, May 29-31, **2013** (oral presentation).
- C3. Organometallic compounds - unusual species stabilized through intramolecular coordination, C. Silvestru, at *The 13<sup>th</sup> Edition of Timișoara's Academic Days*, Timișoara, June 13, **2013** (invited plenary lecture).
- C4. Main Group organometallics – from molecular species to inorganic polymers, C. Silvestru, at *Iași's Academic Days – A XXIV-a Sesiune de Comunicări Științifice a Institutului de Chimie Macromoleculară „Petru Poni”*, October 3-5, **2013** (invited plenary lecture).

### Scientific objectives for phase 2014

In addition to current administrative works (reagents and consumables as well as equipment acquisitions), in this phase of the project were finalized the studies on new compounds with organobismuth(III), -antimony(III) and antimony(V) anions,  $[\{2,6-(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3\}\text{Se}]^+[\text{R}'_2\text{MCl}_{n+1}]^-$  [ $\text{R}' = 2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4$ ,  $n = 1$ ,  $\text{M} = \text{Sb}$ ,  $\text{Bi}$ ;  $\text{R}' = \text{Ph}$ ,  $\text{M} = \text{Sb}$ ,  $n = 1$  or  $n = 3$ ] [*Organoselenium(II) halides containing the pincer 2,6-(Me<sub>2</sub>NCH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub> ligand – an experimental and theoretical investigation*, A. Pop, A. Silvestru, E. J. Juárez-Pérez, M. Arca, V. Lippolis, C. Silvestru, *Dalton Trans.*, **2014**, 43, 2221-2233; DOI: 10.1039/C3DT52886C], as well as those on palladium(II) complexes with chiral, hypervalent organoantimony(III) derivatives of the type  $[2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4]\text{PhSbCl}$  and  $[2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4]\text{Mes}_2\text{Sb}$  [*Palladium(II) complexes with chiral organoantimony(III) ligands. Solution behavior and solid state structures*, D. Copolovici, F. Isaia, H. J. Breunig, C. I. Raț, C. Silvestru, *RSC Advances*, **2014**, 4, 26569-26576; DOI: 10.1039/c4ra03482a].

Studies on organoantimony(III) compounds with chirality induced at the metal centre by intramolecular coordination were continued. For two compounds prepared within the previous phases of the project, i.e. (5) and (6), the molecular structure was established by single-crystal X-ray diffraction (Figure 8).

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Figure 8. Molecular structure of compounds

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(5) and

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(6).

The following exploratory studies were carried out in order to obtain the target compounds:

#### Studies on the catalytic activity of compounds of the type $(\text{R}_2\text{M})_2\text{O}$ , $(\text{RMO})_n$ ( $\text{M} = \text{Sb}$ , $\text{Bi}$ )

##### Synthesis and characterization of organopnictogen oxides and alkoxides

Oxides of the type  $(\text{R}_2\text{M})_2\text{O}$  were prepared from the corresponding bromides  $[2-(^i\text{Pr}_2\text{NCH}_2)\text{C}_6\text{H}_4]_2\text{MBr}$  [ $\text{M} = \text{Sb}$  (**51a**),  $\text{Bi}$  (**51b**)]. The bromides used as starting materials and the oxides  $[\{2-(^i\text{Pr}_2\text{NCH}_2)\text{C}_6\text{H}_4\}_2\text{M}]_2\text{O}$  [ $\text{M} = \text{Sb}$  (**51c**),  $\text{Bi}$

(51d)] were fully characterized by NMR spectroscopy, mass spectroscopy and single-crystal X-ray diffraction (for the bromides – Figure 9). Due to the bulky substituents on nitrogen, only one of the pendant arms is involved in an intramolecular interaction with the metal atom, thus resulting in a distorted *pseudo*-trigonal bipyramidal coordination geometry.

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Figure 9. Molecular structures of the bromides

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(51a) and

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(51b).

Studies were carried out on the reactivity of the cyclic oxide [ $\{2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4\}\text{SbO}\}_3$ ] towards acetic acid, sulfonic acids, phenols and thiophenols in order to obtain new organoantimony(III) compounds with potential to activate small molecules. While the reactions with sulfonic acids, phenol and thiophenol  $\text{C}_6\text{F}_5\text{SH}$  failed to produce the desired compounds, the reactions with acetic acid and  $\text{C}_6\text{F}_5\text{OH}$  gave the new species

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(52) and

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(53). They were investigated spectroscopically (multinuclear NMR, MS) and the

molecular structure of 53 was established by single-crystal X-ray diffraction (Figure 10).

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Figure 10. Molecular structure of

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(53).

Studies were performed on the synthesis of organometallic oxides, alkoxides and aryloxides containing an aromatic ligand with two pendant arms. The dichlorides [M = Sb (54), Bi (55)] and  $[2,6-\{\text{MeN}(\text{CH}_2\text{CH}_2)_2\text{NCH}_2\}_2\text{C}_6\text{H}_3]\text{MCl}_2$  [M = Sb (56), Bi (57)] were prepared and fully characterized from spectroscopic point of view. The molecular structure of the dichlorides 55 and 56 was established by single-crystal X-ray diffraction (Figure 11). The dichlorides 56 and 57 were used as starting materials for the preparation of oxides of the type  $(\text{RMO})_2$  as well as the synthesis of chelate alkoxides/aryloxides, potential candidates for  $\text{CO}_2$  caption (Schemes 2 and 3). The oxides *ciclo*- $[2,6-\{\text{MeN}(\text{CH}_2\text{CH}_2)_2\text{NCH}_2\}_2\text{C}_6\text{H}_3]_2\text{Sb}_2\text{O}_2$  (58) and *ciclo*- $[2,6-\{\text{MeN}(\text{CH}_2\text{CH}_2)_2\text{NCH}_2\}_2\text{C}_6\text{H}_3]_2\text{Bi}_2\text{O}_2$  (67) were isolated as white, crystalline solids. They were investigated spectroscopically (multinuclear NMR, MS) and their molecular structure was established by single-crystal X-ray diffraction (Figure 12).

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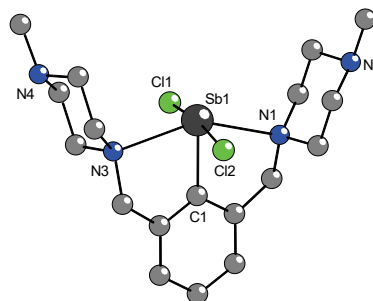


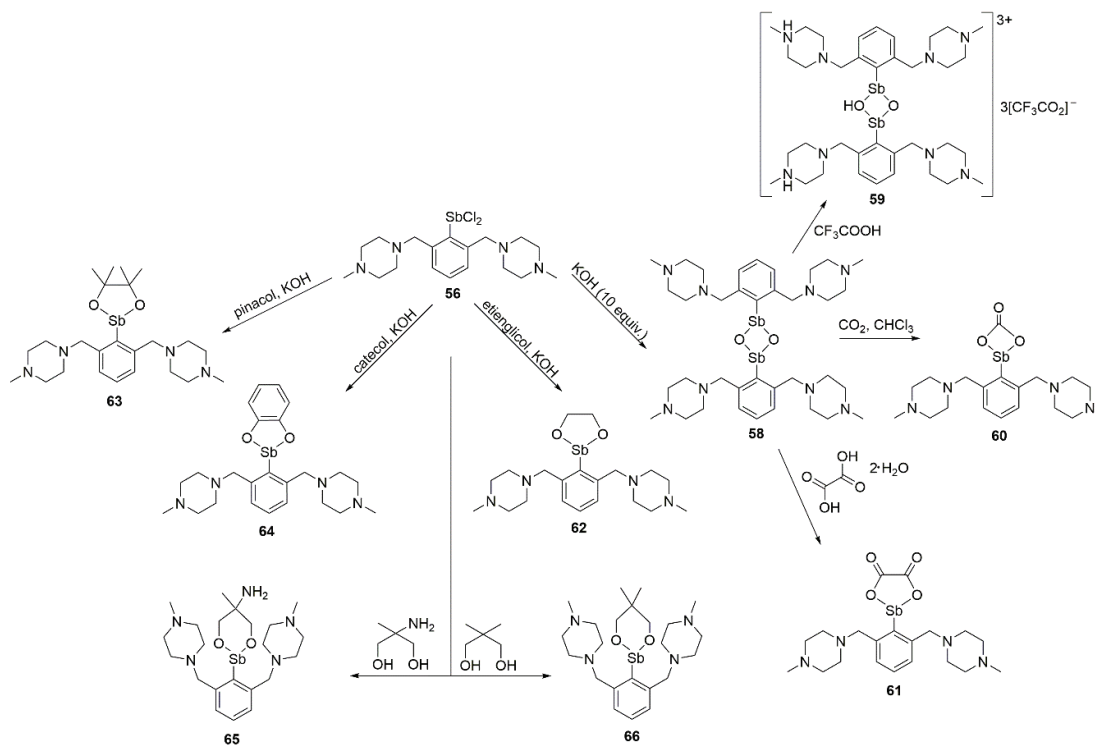
Figure 11. Molecular structures of

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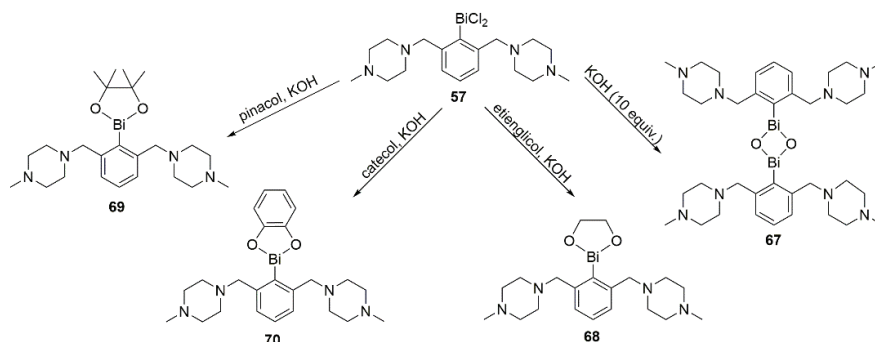
(55), and

(b)  $[2,6-\{\text{MeN}(\text{CH}_2\text{CH}_2)_2\text{NCH}_2\}_2\text{C}_6\text{H}_3]\text{SbCl}_2$  (56).

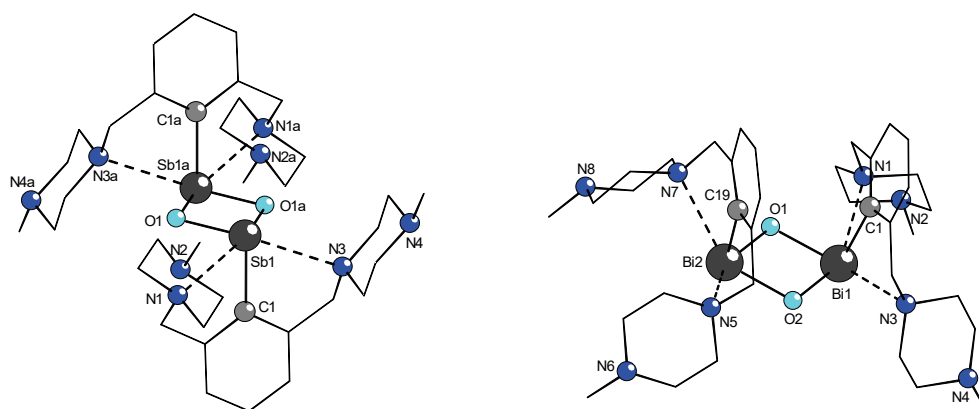




**Scheme 2**



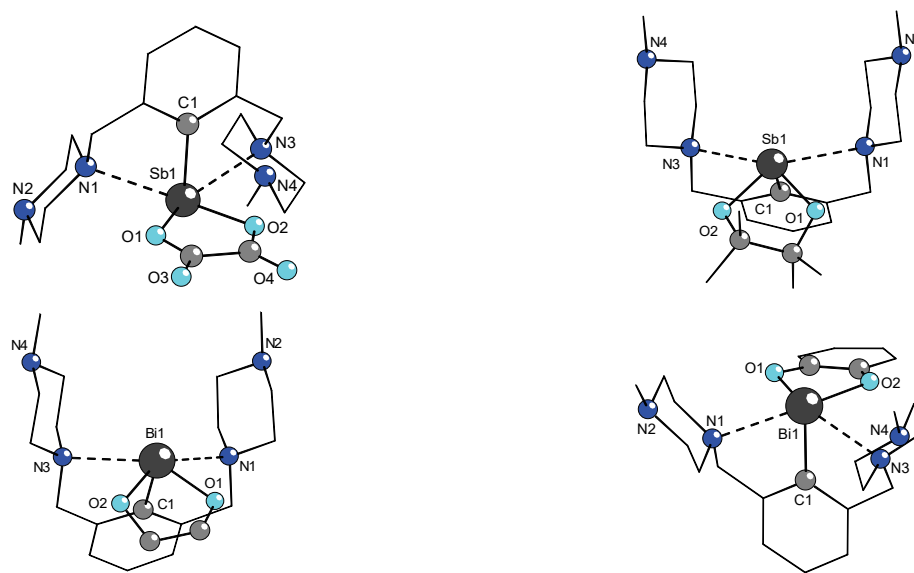
**Scheme 3**



**Figure 12.** Molecular structures of *ciclo*-[2,6-{MeN(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NCH<sub>2</sub>}<sub>2</sub>C<sub>6</sub>H<sub>3</sub>]<sub>2</sub>Sb<sub>2</sub>O<sub>2</sub> (**58**), and *ciclo*-[2,6-{MeN(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NCH<sub>2</sub>}<sub>2</sub>C<sub>6</sub>H<sub>3</sub>]<sub>2</sub>Bi<sub>2</sub>O<sub>2</sub> (**67**).

All the other compounds (Schemes 2 and 3) were isolated as white crystalline solids, stable in air. They were characterized using complex NMR studies, in addition to IR spectroscopy and mass spectrometry. For compounds [ $\{2,6-(\text{MeN}\{\text{CH}_2\text{CH}_2\}_2\text{NCH}_2\}_2\text{C}_6\text{H}_3\}_2\text{Sb}_2\text{O}_2(\text{H})_3](\text{O}_2\text{CCF}_3)_3$  (**59**),  $[2,6-(\text{MeN}(\text{CH}_2\text{CH}_2)_2\text{NCH}_2)_2\text{C}_6\text{H}_3]\text{M}(\text{OCH}_2)_2$  [ $\text{M} = \text{Sb}$  (**62**),  $\text{Bi}$  (**68**)],  $[2,6-(\text{MeN}(\text{CH}_2\text{CH}_2)_2\text{NCH}_2)_2\text{C}_6\text{H}_3]\text{Sb}(\text{OCMe}_2)_2$  (**63**),  $[2,6-(\text{MeN}(\text{CH}_2\text{CH}_2)_2\text{NCH}_2)_2\text{C}_6\text{H}_3]\text{M}(\text{O}-1,2-\text{C}_6\text{H}_4)$  [ $\text{M} = \text{Sb}$  (**64**),  $\text{Bi}$  (**70**)] and  $[2,6-(\text{MeN}(\text{CH}_2\text{CH}_2)_2\text{NCH}_2)_2\text{C}_6\text{H}_3]\text{Sb}[\text{O}(\text{O})\text{CC}(\text{O})\text{O}]$  (**61**) the molecular structure

was established by single-crystal X-ray diffraction (Figure 13). The results obtained in the study of these organopnicogen(III) derivatives are the subject of an article published in 2015 (G. Strîmb, A. Pöllnitz, C. I. Raț and C. Silvestru, *Dalton Trans.*, **2015**, 44, 9927-9942; DOI: 10.1039/c5dt00603a).



**Figure 13.** Molecular structures of (a) [2,6-{MeN(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NCH<sub>2</sub>}<sub>2</sub>C<sub>6</sub>H<sub>3</sub>]<sub>2</sub>Sb[O(O)CC(O)O] (**61**), (b) [2,6-{MeN(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NCH<sub>2</sub>}<sub>2</sub>C<sub>6</sub>H<sub>3</sub>]<sub>2</sub>Sb(OCMe<sub>2</sub>)<sub>2</sub> (**63**), (c) [2,6-{MeN(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NCH<sub>2</sub>}<sub>2</sub>C<sub>6</sub>H<sub>3</sub>]<sub>2</sub>Bi(OCH<sub>2</sub>)<sub>2</sub> (**68**), and (d) [2,6-{MeN(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NCH<sub>2</sub>}<sub>2</sub>C<sub>6</sub>H<sub>3</sub>]<sub>2</sub>Bi(O<sub>2</sub>-1,2-C<sub>6</sub>H<sub>4</sub>) (**70**).

Two phenols with terphenyl backbone, 2,4,6-R<sub>3</sub>C<sub>6</sub>H<sub>2</sub>OH [R = 2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub> (**71**), Me<sub>5</sub>C<sub>6</sub> (**72**)], were prepared using Kumada coupling reactions between 2,4,6-I<sub>3</sub>C<sub>6</sub>H<sub>2</sub>OH and the corresponding Grignard reagent. These phenols will be used in the synthesis of organopnicogen derivatives. Both compounds were characterized using multinuclear NMR spectroscopy and HRMS, and their molecular structure was established by single-crystal X-ray diffraction. The results obtained in the study of these bulky phenols are the subject of an article published in 2015 (A. B. Șolea, M. Olaru, C. Silvestru and C. I. Raț, *Z. Naturforsch., B: Chem. Sci.*, **2015**, 70, 77-81; DOI: 10.1515/znB-2014-0180).

#### **Screening of the capacity to react with CO<sub>2</sub> and preliminary studies on the catalytic activity**

Preliminary studies were performed on the capacity of some organobismuth(III) and -antimony(III) oxides to react with CO<sub>2</sub> and to catalyze reactions between epoxides and CO<sub>2</sub> to give organic polycarbonates and/or cyclic carbonates.

The carbonate **60** was obtained by passing gaseous CO<sub>2</sub> through a solution of the oxide **58** in chloroform. Attempts to obtain **60** from the dichloride **56** and caesium carbonate failed, only the oxide **58** being isolated. No CO<sub>2</sub> absorption by the alkoxide **62** in chloroform was observed.

The carbonate **63** was also screened as catalyst for the reaction of epoxides and CO<sub>2</sub>. To develop this type of studies a specific infrastructure is required to allow experiments at high pressure and this will be a priority for the next phase of the project.

The organobismuth(III) alkoxides **68** – **70** were also screened as CO<sub>2</sub> activators and the reactions were monitored by NMR spectroscopy.

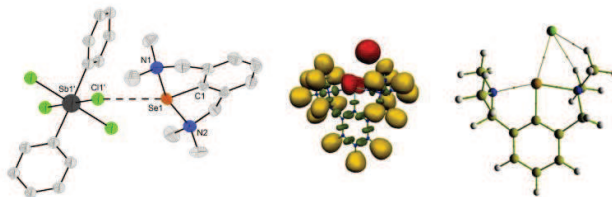
#### **Studies on the catalytic activity of hypervalent compounds of the type [R<sub>2</sub>M]<sup>+</sup>X<sup>-</sup> in Mannich reactions**

The studies on the catalytic activity of some new cationic, hypervalent organoantimony(III) species in the case of the “one-pot” Mannich reactions were continued.

The influence of the solvent was investigated. The compounds screened proved to be useful to catalyze such reaction to build new C-C bonds. The catalytic activity of our compounds was compared with that of a compound reported in the literature,  $C_6H_{11}N(C_6H_4CH_2)_2SbOSO_2CF_3$  (Table 1). Evidences were obtained with respect to the stability of an organoantimony catalyst and to the possibility for repeat use without loss of the catalytic activity in the Mannich system tested.

### Publications appeared in 2014

1. **Organoselenium(II) halides containing the pincer 2,6-(Me<sub>2</sub>NCH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub> Ligand – an experimental and theoretical investigation,**  
A. Pop, A. Silvestru, E. J. Juárez-Pérez, M. Arca, V. Lippolis and C. Silvestru,  
*Dalton Trans.*, **2014**, 43, 2221-2233.  
DOI: 10.1039/C3DT52886C



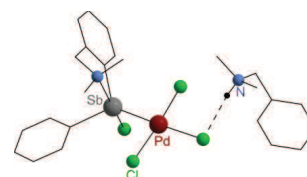
### ABSTRACT

New organoselenium(II) halides of the type  $[RSe]^+X^-$  [ $R = 2,6-(Me_2NCH_2)_2C_6H_3$ ;  $X = Cl$  (**2**),  $Br$  (**3**),  $I$  (**4**)] were prepared by cleavage of the Se–Se bond in  $R_2Se_2$  (**1**) with  $SO_2Cl_2$  followed by halogen exchange when organoselenium chloride was treated with NaBr or KI. The reaction between **2** and  $R'_2MCl_n$  resulted in new ionic  $[RSe]^+[R'_2MCl_{n+1}]^-$  [ $R' = 2-(Me_2NCH_2)C_6H_4$ ,  $n = 1$ ,  $M = Sb$  (**5**),  $Bi$  (**6**);  $R' = Ph$ ,  $M = Sb$ ,  $n = 1$  (**7**) or  $n = 3$  (**8**)] species. All new compounds were investigated in solution by multinuclear NMR spectroscopy ( $^1H$ ,  $^{13}C$ ,  $^{77}Se$ , 2D experiments) and mass spectrometry. The ionic nature of **2** and the antimonates species was confirmed by conductivity studies. The molecular structures of  $[(2,6-(Me_2NCH_2)_2C_6H_3)Se]^+Cl^- \cdot nH_2O$  (**2**· $H_2O$  and **2**· $2H_2O$ ) and  $[(2,6-(Me_2NCH_2)_2C_6H_3)Se]^+[Ph_2SbCl_4]^-$  (**8**), respectively, were established by single-crystal X-ray diffraction, pointing out that the ionic nature of these compounds is also preserved in the solid state, with both nitrogen atoms strongly *trans* coordinated to the selenium atom of the cation. Theoretical calculations carried out at the DFT level were exploited to investigate the nature of the bonding in compounds **2–4** and the free cation  $[RSe]^+$  (**2a**). A topological analysis based on the theory of Atoms-in-Molecules (AIM) and Electron Localization Function (ELF) jointly to a Natural Bond Orbital (NBO) approach was used to shed light on the effect of the nature of the halogen species  $X$  on the bonding within the 3c–4e N–Se–N moiety.

2. **Palladium(II) complexes with chiral organoantimony(III) ligands. Solution behavior and solid state structures,**  
D. Copolovici, F. Isaia, H. J. Breunig, C. I. Raț and C. Silvestru,  
*RSC Advances*, **2014**, 4, 26569-26576.  
DOI: 10.1039/c4ra03482a

### ABSTRACT

The chiral compound  $(2-Me_2NCH_2C_6H_4)PhSbCl_2$  (**1**) was obtained from  $(2-Me_2NCH_2C_6H_4)Li$  and  $PhSbCl_2$  in 1 : 1 molar ratio, while  $(2-Me_2NCH_2C_6H_4)Mes_2Sb$  (**2**) was prepared from  $(2-Me_2NCH_2C_6H_4)SbCl_2$  and  $MesMgBr$  in 1 : 2 molar ratio. The compounds **1** and **2** were used to obtain the Pd(II)/stibine complexes:  $[Me_2NHCH_2C_6H_5]^+[PdCl_3(SbCl(Ph)(C_6H_4CH_2NMe_2-2)-Sb)]^-$  (**3**) and  $[PdCl_2(SbMes_2(C_6H_4CH_2NMe_2-2)-N,Sb)]$  (**4**). All the compounds were characterized by multinuclear NMR spectroscopy in solution, elemental analysis, mass spectrometry and single-crystal X-ray diffraction studies. In compounds **1–3** the coordination geometry around the antimony atom is pseudo-trigonal bipyramidal, while in compound **4** a tetrahedral geometry around the antimony atom is observed. Theoretical calculations at the DFT level on compounds **1–4** were used in order to gain insight into the nature of the coordinative bonds.



### Contributions to national and international conferences

- C1. Chelated antimony(III) and bismuth(III) alkoxides,  
A. Pöllnitz, G. Strîmb, C. Silvestru,  
at *The 5<sup>th</sup> EuCheMS Chemistry Congress*, Istanbul (Turkey), August 31 - Septembrie 4, **2014** (poster).

- C2. New hypervalent organoantimony(III) and -bismuth(III) compounds,  
I. Chircă, A. M. Preda, C. Silvestru,  
 at *A XXXIII Conferință Națională de Chimie*, Căciulata, Octombrie 1-3, **2014** (poster).
- C3. Syntheses and structural characterization of organoantimony(III) compounds with 2-(Ph<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub> and 2-[Mes(Me)NCH<sub>2</sub>]C<sub>6</sub>H<sub>4</sub> substituents,  
G. Strîmb, C. I. Raț, C. Silvestru,  
 at *A XXXIII Conferință Națională de Chimie*, Căciulata, Octombrie 1-3, **2014** (poster).

### Scientific objectives for phase 2015

In the phase 2015 of this project, besides current management activities (acquisition of reagents, solvents and other materials, small equipments), some of the studies started in the previous phases were completed, *i.e.*:

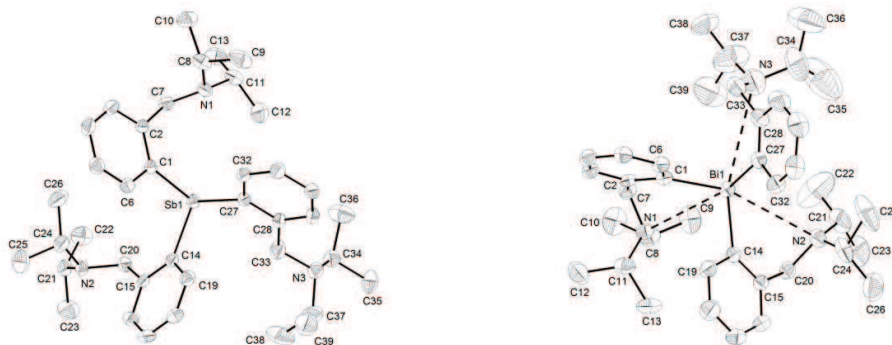
(i) the synthesis of organoantimony(III) and -bismuth(III) oxides, alkoxides and aryloxides containing a organic group with two pendant arms, *i.e.* 2,6-{MeN(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NCH<sub>2</sub>}<sub>2</sub>C<sub>6</sub>H<sub>3</sub>. All compounds were spectroscopically characterized in solution by multinuclear NMR (including studies at variable temperature), and in most cases the molecular structure was established by single-crystal X-ray diffraction. Hexamer clusters of water molecules with a [tetramer + 2] structure (two water molecules connected to the opposite corners of a square planar tetramer of water molecules) were evidenced for the first time in the crystal of the oxide [*ciclo-syn*-{2,6-{MeN(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NCH<sub>2</sub>}<sub>2</sub>C<sub>6</sub>H<sub>3</sub>}<sub>2</sub>Bi<sub>2</sub>O<sub>2</sub>·4H<sub>2</sub>O)]<sub>n</sub>. Theoretical calculations were carried out in order to evaluate the stabilization energy due to the intramolecular coordination of the pendant arms, the degree of association and the formation energy of the studied organopnicogen compounds. The results were reported in an article published in the prestigious journal *Dalton Transactions* - G. Strîmb, A. Pöllnitz, C. I. Raț and C. Silvestru, *Dalton Trans.*, **2015**, 44, 9927-9942; DOI: 10.1039/c5dt00603a.

(ii) phenols with a terphenyl backbone, 2,4,6-R<sub>3</sub>C<sub>6</sub>H<sub>2</sub>OH [R = 2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub> (**71**), Me<sub>3</sub>C<sub>6</sub> (**72**)], which will be used in the synthesis of organopnicogen derivatives. The results obtained are the subject of an article published in the journal *Z. Naturforsch., B: Chem. Sci.* - A. B. Şolea, M. Olaru, C. Silvestru and C. I. Raț, *Z. Naturforsch., B: Chem. Sci.*, **2015**, 70, 77-81; DOI: 10.1515/znb-2014-0180.

(iii) ionic compounds with diorganoantimony(III) cations stabilized through intramolecular coordination and their conversion to diorganoantimony(III) fluorides; the preparation method of these fluorides is an original and general one, at least in the case of compounds containing an organic group with a pendant arm capable of intramolecular coordination. The results obtained are the subject of an article published in the journal *RSC Advances* - A. M. Preda, C. I. Raț, C. Silvestru, H. Lang, T. Rüffer and M. Mehring, *RSC Advances*, **2015**, 5, 99832-99840; DOI: 10.1039/c5ra21788a.

(iv) new organic proligands with a chiral nitrogen atom, *i.e.* 2-(MesNHCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>Br (**73**), 2-[Mes(Me)NCH<sub>2</sub>]C<sub>6</sub>H<sub>4</sub>Br (**2**) si 2-[Mes{(O)CH}NCH<sub>2</sub>]C<sub>6</sub>H<sub>4</sub>Br (**74**), which can be utilized for the preparation of chiral organometallic species. The compounds were characterized by multinuclear NMR and IR spectroscopy, and mass spectrometry. The molecular structure of 2-[Mes{(O)CH}NCH<sub>2</sub>]C<sub>6</sub>H<sub>4</sub>Br was established by single-crystal X-ray diffraction. The results obtained are the subject of an article published in the journal *Revue Roumaine de Chimie* – G. Strîmb, C. I. Raț and C. Silvestru, *Rev. Roum. Chim.*, **2015**, 60, 651-657. (Nr. omagial Valer FARCASAN).

(v) two new homoleptic triorganopnicogen(III) derivatives, [2-(<sup>i</sup>Pr<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>]<sub>3</sub>M [M = Sb (**75**), Bi (**76**)], obtained by reacting [2-(<sup>i</sup>Pr<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>]MgBr (prepared *in situ* from [2-(<sup>i</sup>Pr<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>]Br and Mg) with MCl<sub>3</sub>.



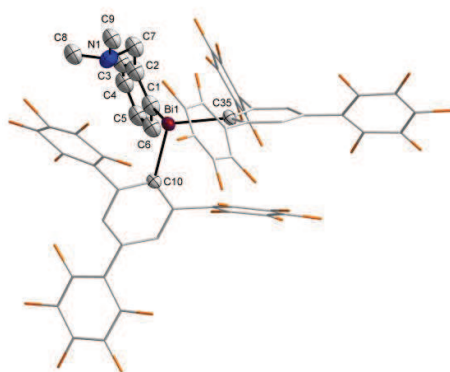
**Figure 14.** Molecular structure of compounds [2-(<sup>i</sup>Pr<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>]<sub>3</sub>Sb (**75**) and [2-(<sup>i</sup>Pr<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>]<sub>3</sub>Bi (**76**).

The compounds were characterized by multinuclear NMR spectroscopy in solution and single-crystal X-ray diffraction. The NMR data in solution are consistent with equivalent organic substituents attached to the metal atom,



while in solid state there are significant differences: the pendant arms in the antimony derivative are twisted to push the nitrogen atoms far from the central atom (Figure 14,a), while in the bismuth analogue there are weak N→Bi intramolecular interactions (Figure 14,b), resulting in a distorted octahedral coordination geometry in the (C,N)<sub>3</sub>Bi core. The results obtained are the subject of an article published in the journal *Revue Roumaine de Chimie* - I. Chircă, A. Soran, A. Silvestru and C. Silvestru, *Rev. Roum. Chim.*, **2015**, *60*, 643-650. (Nr. omagial Valer FARCASAN).

The studies on the chiral derivatives with fluoro-organic groups attached to a bismuth atom were extended with the synthesis of the compound [2-(Me<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>][2,4,6-(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>]<sub>2</sub>Bi (**77**), obtained by reacting [2-(Me<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>]BiBr<sub>2</sub> and 2,4,6-(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>Li, in 1:2 molar ratio. The compound was characterized by multinuclear NMR spectroscopy in solution and single-crystal X-ray diffraction (Figure 15). In contrast to [2-(Me<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>](C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>Bi (**30**), which is sensitive to oxygen and moisture, the compound [2-(Me<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>][2,4,6-(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>]<sub>2</sub>Bi is stable to air and water, in spite of the presence of an electron deficient organic groups. This behavior is due to the increased kinetic stability as result of the steric protection offered by terphenyl substituents. This protection is also suggested by the <sup>13</sup>C and <sup>19</sup>F NMR spectra which indicate that the free rotation of the C<sub>6</sub>F<sub>5</sub> groups in the positions 2 and 6 of the terphenyl ligand is blocked. The results obtained in the study of the chiral species with C<sub>6</sub>F<sub>5</sub> groups attached to a bismuth atom are the subject of an article published in the prestigious journal *Dalton Transactions* - M. Olaru, M. Nema, A. Soran, H. J. Breunig and C. Silvestru, *Dalton Trans.*, **2016**, *45*, 9419-9428; DOI: 10.1039/C5DT05074J.





They were isolated as white solids, stable in air at room temperature. The identity of the compounds was confirmed by multinuclear NMR spectroscopy in solution and the molecular structure of some representative compounds was established by single-crystal X-ray diffraction. Dimer associations through O→Sb intermolecular interactions were observed in the crystal of such compounds; the metal centre becomes pentacoordinated, with a distorted trigonal bipyramidal geometry (Figure 16).

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**Figure 16.** Dimer associations through O→Sb interactions: (a) (b) (78) and (79).

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These compounds will be tested for their reactivity towards CO<sub>2</sub> as well as their catalytic properties in various reactions. The studies performed so far within this project on the catalytic activity of the obtained organoantimony(III) and – bismuth(III) compounds for the synthesis of cyclic carbonates and/or polycarbonates from CO<sub>2</sub> were not conclusive.

The studies regarding the catalytic properties of some cationic, hypervalent organoantimony(III) compounds for the “one-pot” Mannich reaction were continued. The organoantimony(III) compounds exhibit Lewis acidity due to the presence of empty *d* orbitals at the metal centre. This Lewis acid character can be increased by cations generation (*see*: A. P. M. Robertson, P. A. Gray, N. Burford, *Angew. Chem. Int. Ed.* **2014**, *53*, 6050-6069). Due to the Lewis acid character the organoantimony(III) cations might have a similar behavior as the catalytic proton in the Mannich reactions. Therefore, two main objectives were considered, *i.e.* the generation of some stable diorganoantimony(III) cations and the screening of their catalytic properties.

(i) **Generation of diorganoantimony(III) cations**

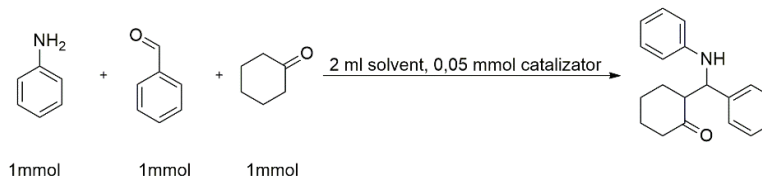
The organoantimony(III) cations can be obtained by reacting an organoantimony(III) halide with the salt of an anion with weak coordination properties as, for example Ag[SbF<sub>6</sub>], Tl[PF<sub>6</sub>], Ag[BF<sub>4</sub>], Na[BAr<sup>F</sup><sub>4</sub>]; Ar<sup>F</sup> = 3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>). Several attempts were carried out and after the separation of the insoluble silver(I) or thallium(I) halides, the obtained new organoantimony(III) species were characterized by multinuclear (<sup>1</sup>H, <sup>19</sup>F) NMR spectroscopy in solution. In some cases the nature of the organometallic products obtained are still under investigation.

The reaction between [2-(Me<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>]<sub>2</sub>SbCl and was carried out in different anhydrous solvents (toluene, MeCN) in opened atmosphere or under inert atmosphere. After working up the reaction mixture the desired compound, (81), was isolated. Similarly were prepared (82) and (83). The reaction between [2-(Me<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>]<sub>2</sub>SbCl and in THF yielded (84) as a yellowish solid. The identity of all these compounds was confirmed by multinuclear RMN (<sup>1</sup>H, <sup>19</sup>F) spectroscopy.

The <sup>19</sup>F RMN spectrum of the reaction mixture obtained by reacting [2-(Me<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>]<sub>2</sub>SbCl and in CDCl<sub>3</sub>, exhibits only one resonance signal, thus suggesting the formation of the desired compound, (85).

(ii) **Studies on the catalytic effect of diorganostibiu(III) cations on Mannich reactions**

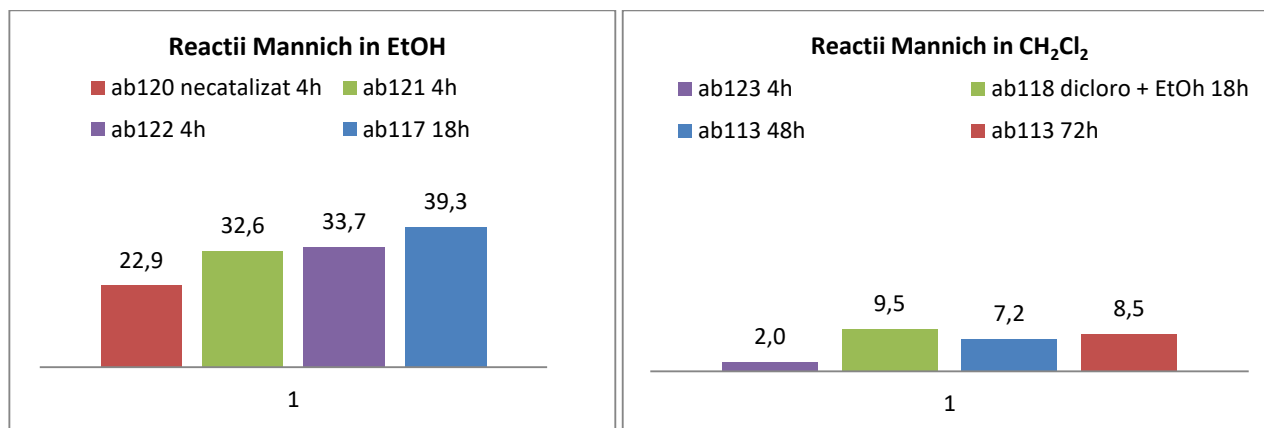
The catalytic screenings were performed for a typical Mannich reaction between aniline, benzaldehyde and cyclohexanone in 1:1:1 molar ratio (Scheme 5), using a certain amount of catalyst, in various solvents, at room temperature.



**Scheme 5**

The reactions were monitored for 4 hours by chromatography, followed by the work-up of the reaction mixture. The crude products were analyzed by GC/MS, after the separation of the catalyst. The best results were obtained using a protic solvent (Chart 1). The screened compounds proved to be useful for the formation of a C-C bond in the tested system.

**Chart 1** Yields of a Mannich reaction catalyzed by a ionic diorganoantimony(III) compound in a protic and an aprotic solvent



### Transition metal complexes with triorganostibines – potential catalysts in coupling reactions

Several new Cu(I) and Pd(II) complexes with carbenes and triorganostibines were prepared (Scheme 6) in order to perform their screening as catalysts in coupling reactions. The Cu(I) and Pd(II) complexes with carbenes were isolated as white and yellow solids, respectively. They were used as starting materials for new complexes containing triorganostibines. Ionic Cu(I) and neutral Pd(II) complexes containing both carbene and R<sub>3</sub>Sb as ligands were isolated. During the next phases of the project the potential catalytic activity of some of the obtained transition metal complexes will be screened in coupling reactions.

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The compounds Babes-Bolyai University  
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CONFIDENTIAL (86) or the neutral complexes Babes-Bolyai University  
CONFIDENTIAL (87) and Babes-Bolyai University  
CONFIDENTIAL (88), potential catalysts for coupling reactions.

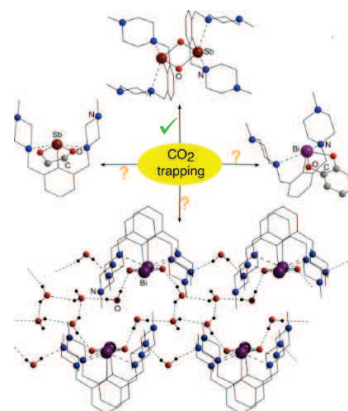
Complexes of palladium with bulky isocyanide ligands as 2,4,6-Mes<sub>3</sub>C<sub>6</sub>H<sub>2</sub>NC and 2,4,6-(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>NC were prepared and structurally characterized by NMR spectroscopy in solution, IR spectroscopy, mass spectrometry, and the molecular structure of two representative complexes was established by single-crystal X-ray diffraction. These complexes can be used further as starting materials for the preparation of complexes containing triorganostibines, with potential use as catalysts. Part of the obtained results were presented within the conference *Zilele Academice Iesene - A XXV-a Sesiune de Comunicări Stiintifice a Institutului de Chimie Macromoleculară „Petru Poni”*, Iasi, September 24-26, 2015 (*Palladium Coordination Compounds with Bulky Isocyanide Ligands*, K. T. Kegyes, M. Olaru, C. Silvestru, C. I. Rat).

### Publications appeared in 2015

1. **A general route to monoorganopnictogen(III) (M = Sb, Bi) compounds with a pincer (N,C,N) group and oxo ligands,**  
G. Strîmb, A. Pöllnitz, C. I. Raț and C. Silvestru,  
*Dalton Trans.*, **2015**, 44, 9927-9942.  
DOI: 10.1039/c5dt00603a

## ABSTRACT:

The reaction of  $\text{RMCl}_2$  [ $\text{R} = 2,6\text{-}[\text{MeN}(\text{CH}_2\text{CH}_2)_2\text{NCH}_2]_2\text{C}_6\text{H}_3$ ;  $\text{M} = \text{Sb}$  (1),  $\text{Bi}$  (2)] with  $\text{KOH}$  affords the isolation of the oxides *cyclo*- $\text{R}_2\text{M}_2\text{O}_2$  [ $\text{M} = \text{Sb}$  (3),  $\text{Bi}$  (4)]. Treatment of 3 with trifluoroacetic acid produced an ionic species (5) with a dinuclear cation that contains organic ligands protonated partially at one of the pendant arms. The cyclic oxide 3 is able to trap gaseous  $\text{CO}_2$  to give “ $\text{RSbCO}_3$ ” (6), the degree of oligomerization being under investigation. The reactivity of the dinuclear oxide 3 was also investigated towards oxalic acid or dopamine hydrochloride and pure mononuclear compounds could be isolated, *i.e.*  $\text{RSb}[\text{O}(\text{O})\text{CC}(\text{O})\text{O}]$  (7) and  $\text{RSb}[\text{O}_2\text{-}1,2\text{-C}_6\text{H}_3\text{-}3\text{-(CH}_2)_2\text{NH}_2]\text{Cl}$  (8). The reaction of the dichlorides 1 and 2 with ethylene glycol, pinacol or catechol, in presence of  $\text{KOH}$ , led to 2-organo-1,3,2-dioxastibolanes or -bismolanes  $\text{RM}(\text{OCH}_2)_2$  [ $\text{M} = \text{Sb}$  (9),  $\text{Bi}$  (10)],  $\text{RM}(\text{OCMe}_2)_2$  [ $\text{M} = \text{Sb}$  (11),  $\text{Bi}$  (12)] and 2-organo-1,3,2-dioxastibole or -bismole  $\text{RM}(\text{O}_2\text{-}1,2\text{-C}_6\text{H}_4)$  [ $\text{M} = \text{Sb}$  (13),  $\text{Bi}$  (14)], respectively. The compounds were investigated by NMR spectroscopy, including variable temperature experiments, providing evidences for the presence of the intramolecular  $\text{N} \rightarrow \text{M}$  interactions in solution. Single crystal X-ray diffraction studies were performed for most compounds and revealed an organic group  $\text{R}$  acting as a pincer ligand resulting in a distorted square pyramidal ( $\text{N,C,N})\text{MO}_2$  core with *cis* intramolecular  $\text{N} \rightarrow \text{M}$  interactions placed in *trans* to  $\text{M}-\text{O}$  bonds. This contrasts to the  $\text{N} \rightarrow \text{M}$  interactions *trans* to each other as found in the  $\text{RMCl}_2$  used as starting materials. The crystals of the oxides 3 and  $4 \cdot 4\text{H}_2\text{O}$  contain different geometric isomers with *trans* and *cis* orientation of the  $\text{M}-\text{C}$  bonds, respectively, with respect to the planar  $\text{M}_2\text{O}_2$  ring. In the supramolecular polymeric architecture established in the crystal of  $4 \cdot 4\text{H}_2\text{O}$  an important finding is the experimental observation of water hexamer units with a [tetramer+2] structure (water molecules connected to opposite corners of a square water tetramer) fixed between 1D-chains of the type  $(\text{cis-R}_2\text{Bi}_2\text{O}_2 \cdot \text{H}_2\text{O})_n$  through additional hydrogen bonds to oxygen atoms of the dinuclear organobismuth(III) moieties. Theoretical calculations were carried out on 2-14 in order to bring insight in the stabilization energy brought by intramolecular coordination of the pendant arms, association degrees and formation energies of the organopnicogen compounds with chelating ligands.



## 2. Synthesis and structural characterization of substituted phenols with *m*-terphenyl backbone, 2,4,6- $\text{R}_3\text{C}_6\text{H}_2\text{OH}$ ( $\text{R} = 2,4,6\text{-Me}_3\text{C}_6\text{H}_2$ , $\text{Me}_5\text{C}_6$ ),

A. B. Şolea, M. Olaru, C. Silvestru and C. I. Raţ,  
*Z. Naturforsch., B: Chem. Sci.*, **2015**, 70, 77-81.

DOI: 10.1515/znb-2014-0180

**Abstract:** Substituted phenols with a *m*-terphenyl backbone 2,4,6- $\text{R}_3\text{C}_6\text{H}_2\text{OH}$  [ $\text{R} = 2,4,6\text{-Me}_3\text{C}_6\text{H}_2$  (1),  $\text{Me}_5\text{C}_6$  (2)] were synthesized using Kumada cross-coupling reactions between 2,4,6- $\text{I}_3\text{C}_6\text{H}_2\text{OH}$  and the corresponding Grignard reagent. Both compounds were structurally characterized in solution by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy and HRMS. The molecular structures of 1 and 2 were determined by single-crystal X-ray diffraction.

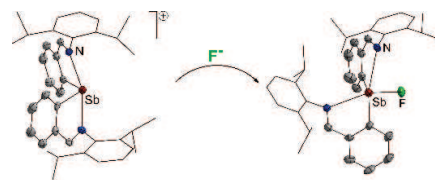
## 3. Hypervalent diorganoantimony(III) fluorides via diorganoantimony(III) cations – a general method of synthesis,

A. M. Preda, C. I. Raţ, C. Silvestru, H. Lang, T. Rüffer and M. Mehring,  
*RSC Advances*, **2015**, 5, 99832-99840.

DOI: 10.1039/c5ra21788a

## ABSTRACT:

Novel diorganoantimony(III) fluorides containing ligands with pendant arms,  $\text{R}_2\text{SbF}$  (5),  $(\text{R})\text{PhSbF}$  (6) [ $\text{R} = 2\text{-(2',6'-}^i\text{Pr}_2\text{C}_6\text{H}_3\text{N=CH)}\text{C}_6\text{H}_4$ ],  $\text{R}''_2\text{SbF}$  (7) and  $(\text{R}'')\text{PhSbF}$  (8) [ $\text{R}'' = 2\text{-(Me}_2\text{NCH}_2)\text{C}_6\text{H}_4$ ], were prepared *via* the ionic derivatives  $[\text{R}_2\text{Sb}]^+[\text{PF}_6]^-$  (1),  $[(\text{R})\text{PhSb}]^+[\text{PF}_6]^-$  (2),  $[\text{R}''_2\text{Sb}]^+[\text{SbF}_6]^-$  (4) and  $[(\text{R}'')\text{PhSb}]^+[\text{SbF}_6]^-$  (obtained *in situ*) by treatment with  $[\text{Bu}_4\text{N}][\text{F} \cdot 3\text{H}_2\text{O}]$ . The ionic species used as starting materials as well as  $[\text{R}'_2\text{Sb}]^+[\text{PF}_6]^-$  (3) [ $\text{R}' = 2\text{-(2',4',6'-Me}_3\text{C}_6\text{H}_2\text{N=CH)}\text{C}_6\text{H}_4$ ] were obtained from the corresponding bromides or chlorides and  $\text{Ti}[\text{PF}_6]_3$  or  $\text{Ag}[\text{SbF}_6]$ . The compounds were investigated by multinuclear NMR spectroscopy in solution, MS and IR spectroscopy in the solid state. The molecular structures of the ionic species 1-2,  $\text{CH}_2\text{Cl}_2$  and 3-2,  $\text{CHCl}_3$  as well as of the fluorides 5-8 were determined by single-crystal X-ray diffraction.



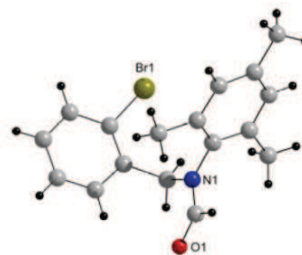
## 4. Synthesis and characterization of 2-[Mes(Me)NCH<sub>2</sub>] $\text{C}_6\text{H}_4\text{Br}$ and 2-[Mes{(O)CH}NCH<sub>2</sub>] $\text{C}_6\text{H}_4\text{Br}$ – Precursors for novel one pendant arm ligands,

G. Strîmb, C. I. Raţ and C. Silvestru,  
*Rev. Roum. Chim.*, **2015**, 60, 651-657. (Nr. omagial Valer FARASAN)



## ABSTRACT:

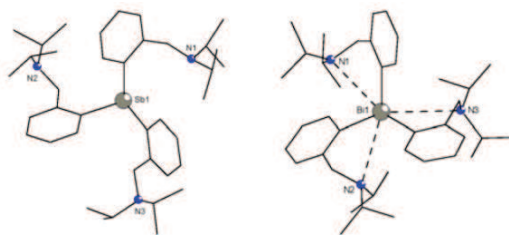
A new secondary amine 2-(MesNHCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>Br (**2**) was synthesized starting from imine 2-(MesN=CH)C<sub>6</sub>H<sub>4</sub>Br (**1**) and NaBH<sub>4</sub>. Reaction of **2** with paraformaldehyde and HC(O)OH gave almost quantitatively 2-[Mes(Me)NCH<sub>2</sub>]C<sub>6</sub>H<sub>4</sub>Br (**3**), while treatment of **2** with paraformaldehyde and CH<sub>3</sub>C(O)OH resulted in **3** as a major product besides a minor amount of the unexpected 2-[Mes{(O)CH}NCH<sub>2</sub>]C<sub>6</sub>H<sub>4</sub>Br (**4**) compound. The compounds were characterized by multinuclear NMR and IR spectroscopy, mass spectrometry and the molecular structure of **4** was established by single-crystal X-ray diffraction.



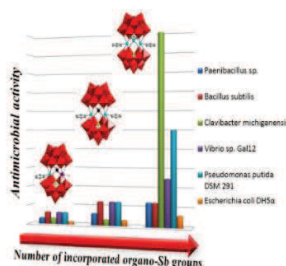
5. **Homoleptic organometallic compounds of heavy pnictogens. Crystal and molecular structure of [2-(<sup>i</sup>Pr<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>]<sub>3</sub>M (M = Sb, Bi),**  
I. Chircă, A. Soran, A. Silvestru and C. Silvestru,  
*Rev. Roum. Chim.*, **2015**, 60, 643-650. (Nr. omagial Valer FARCASAN)

## ABSTRACT:

Two new homoleptic triorganopnictogen(III) species, [2-(<sup>i</sup>Pr<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>]<sub>3</sub>M [M = Sb (**2**), Bi (**3**)] were obtained by reacting [2-(<sup>i</sup>Pr<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>]<sub>3</sub>MgBr (prepared *in situ* from [2-(<sup>i</sup>Pr<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>]<sub>2</sub>MgBr (**1**) and Mg filings] with MCl<sub>3</sub>. The compounds were characterized by multinuclear NMR solution studies and the crystal and molecular structure of **2** and **3** was established by single-crystal X-ray diffraction. The NMR data are consistent with one type of organic group attached to the metal atom in **2** and **3**. The main difference between the molecules of the organometallic species is observed in the solid state. While for the antimony(III) compound all pendant arms are twisted to push the nitrogen atoms far from the metal centre, in the bismuth(III) derivative weak intramolecular N→Bi interactions are established for all three nitrogen atoms, thus increasing the coordination number from three to six in a distorted octahedral (C,N)<sub>3</sub>Bi core.



6. **Organoantimony(III)-containing tungstoarsenates(III): from controlled assembly to biological activity,**  
P. Yang, B. S. Bassil, Z. Lin, A. Haider, G. Alfaro-Espinoza, M. S. Ullrich, C. Silvestru and U. Kortz,  
*Chem. Eur. J.*, **2015**, 21, 15600-15606.  
DOI: 10.1002/chem.201502398

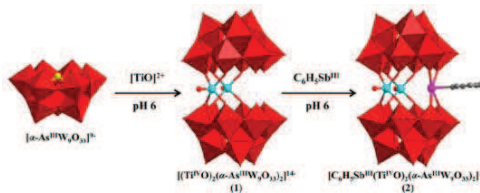


**Abstract:** A family of three sandwich-type, phenylantimony(III)-containing tungstoarsenates(III), [(PhSb<sup>III</sup>){Na(H<sub>2</sub>O)}-As<sup>III</sup><sub>2</sub>W<sub>19</sub>O<sub>67</sub>(H<sub>2</sub>O)]<sup>11-</sup> (**1**), [(PhSb<sup>III</sup>)<sub>2</sub>As<sup>III</sup><sub>2</sub>W<sub>19</sub>O<sub>67</sub>(H<sub>2</sub>O)]<sup>10-</sup> (**2**), and [(PhSb<sup>III</sup>)<sub>3</sub>(B-α-As<sup>III</sup>W<sub>9</sub>O<sub>33</sub>)<sub>2</sub>]<sup>12-</sup> (**3**), have been synthesized by one-pot procedures and isolated as hydrated alkali metal salts, Cs<sub>3</sub>K<sub>3.5</sub>Na<sub>4.5</sub>[(PhSb<sup>III</sup>){Na(H<sub>2</sub>O)}As<sup>III</sup><sub>2</sub>W<sub>19</sub>O<sub>67</sub>(H<sub>2</sub>O)]·41H<sub>2</sub>O (**CsKNa-1**), Cs<sub>4.5</sub>K<sub>5.5</sub>[(PhSb<sup>III</sup>)<sub>2</sub>As<sup>III</sup><sub>2</sub>W<sub>19</sub>O<sub>67</sub>(H<sub>2</sub>O)]·35H<sub>2</sub>O (**CsK-2**), and Cs<sub>4.5</sub>Na<sub>7.5</sub>[(PhSb<sup>III</sup>)<sub>3</sub>(B-α-As<sup>III</sup>W<sub>9</sub>O<sub>33</sub>)<sub>2</sub>]·42H<sub>2</sub>O (**CsNa-3**). The number of incorporated {PhSb<sup>III</sup>} units could be selectively

tuned from one to three by careful control of the reaction parameters. The three compounds were characterized in the solid state by single-crystal XRD, IR spectroscopy, and thermogravimetric analysis. The aqueous solution stability of sandwich polyanions **1–3** was also studied by multinuclear (<sup>1</sup>H, <sup>13</sup>C, <sup>183</sup>W) NMR spectroscopy. Effective inhibitory activity against six different kinds of bacteria was identified for all three polyanions, for which the activity increased with the number of incorporated {PhSb<sup>III</sup>} groups.

7. **Ti<sub>2</sub>-containing 18-tungsto-2-arsenate(III) monolacunary host and the incorporation of a phenylantimony(III) guest,**  
K.-Y Wang, Z. Lin, B. S. Bassil, X. Xing, A. Haider, B. Keita, G. Zhang, C. Silvestru and U. Kortz,  
*Inorg. Chem.*, **2015**, 54, 10530-10532.  
DOI: 10.1021/acs.inorgchem.5b01863

**ABSTRACT:** The novel  $\text{Ti}_3$ -containing, sandwich-type 18-tungsto-2-arsenate(III)  $[(\text{Ti}^{\text{IV}}\text{O})_2(\alpha\text{-As}^{\text{III}}\text{W}_9\text{O}_{33})_2]^{14-}$  (**1**) was successfully synthesized by the reaction of  $[\text{TiO}]^{2+}$  species with  $[\alpha\text{-As}^{\text{III}}\text{W}_9\text{O}_{33}]^{9-}$ . The monolacunary polyanion **1** is solution-stable, and a further reaction with 1 equiv of phenylantimony(III) dichloride resulted in  $[\text{C}_6\text{H}_5\text{Sb}^{\text{III}}(\text{Ti}^{\text{IV}}\text{O})_2(\alpha\text{-As}^{\text{III}}\text{W}_9\text{O}_{33})_2]^{12-}$  (**2**). Both polyanions **1** and **2** were structurally characterized in the solid state and solution. Electrochemical studies were also performed on both polyanions.



### Contributions to national and international conferences

- C1. Palladium coordination compounds with bulky isocyanide ligands, K. T. Kegyes, M. Olaru, C. Silvestru, C. I. Rat, at *Zilele Academice Iesene - A XXV-a Sesiune de Comunicări Stiintifice a Institutului de Chimie Macromoleculară „Petru Poni”*, Iasi, 24-26 septembrie **2015** (prezentare orală).

### Scientific objectives for phase 2016

In the last phase (December 2015- December 2016) of this project, in addition to current management activities (acquisition of reagents, solvents and other materials), some of the studies started in the previous phases were completed, *i.e.*:


(i) Chiral species with fluorinated organic groups attached to bismuth. The results are the subject of an article published in *Dalton Transactions* - M. Olaru, M. Nema, A. Soran, H. J. Breunig and C. Silvestru, *Dalton Trans.*, **2016**, 45, 9419-9428; DOI: 10.1039/C5DT05074J. It should be mentioned here that this paper was selected to illustrate the cover of the corresponding issue of this prestigious journal.

(ii) The research studies developed in collaboration with the group of Prof. Ulrich Kortz (Jacobs Universität, Bremen, Germany) were continued. Several new ionic compounds with discrete heteropolywolframate anion incorporating one up to four  $[2-(\text{Me}_2\text{HN}^+\text{CH}_2)\text{C}_6\text{H}_4]\text{Sb}(\text{III})$ ,  $\text{PhSb}(\text{III})$  or  $(\text{HO})\text{Sb}(\text{III})$  fragments were prepared. The compounds were fully characterized by multinuclear NMR spectroscopy in solution, IR spectroscopy and single-crystal X-ray diffraction. The *in vitro* antibacterial activity was investigated. The results obtained are the subject of two articles published in *Inorganic Chemistry*, a prestigious journal of the American Chemical Society - P. Yang, Z. Lin, G. Alfaro-Espinoza, M. S. Ullrich, C. I. Raț, C. Silvestru and U. Kortz, *Inorg. Chem.*, **2016**, 55, 251-258; DOI: 10.1021/acs.inorgchem.5b02189, and, respectively, P. Yang, Z. Lin, B. S. Bassil, G. Alfaro-Espinoza, M. S. Ullrich, M.-X. Li, C. Silvestru and U. Kortz, *Inorg. Chem.*, **2016**, 55, 3718-3720; DOI: 10.1021/acs.inorgchem.6b001.

(iii) The studies on the catalytic activity of some hypervalent, cationic organoantimony(III) species on “one-pot” Mannich reactions were continued. The catalytic potential of the compound **(84)** was evaluated in the system aniline-benzaldehyde-cyclohexanone, using different protic solvents. The evolution of the reactions was checked by TLC and the yield was established by GS-MS.

A summary of some of the results obtained using as catalysts the compounds **(84)** and  $[\text{S}(\text{CH}_2\text{C}_6\text{H}_4)_2\text{Bi}(\text{H}_2\text{O})][\text{ClO}_4]$  (prepared by us using the method reported in the literature) is shown in Table 2. Such compounds proved to be useful as catalyst for the formation of a C–C bond in the system used.

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To further develop the studies on the catalytic activity of new hypervalent organobismut(III) species with tetrahydrodibenzo[c,f][1,5]azabismocine fragment several new diorganobismuth(III) halides of the type  $[\text{RN}(\text{CH}_2\text{C}_6\text{H}_4)_2]\text{BiX}$  [R =  X = halogen] were prepared, *i.e.* the bromides  $[\text{RN}(\text{CH}_2\text{C}_6\text{H}_4)_2]\text{BiBr}$  (**89-91**) and the species **92-100** (Scheme 7). The compounds were isolated as crystalline solids, soluble in common organic solvents. They were characterized by multinuclear ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{19}\text{F}$ ,  $^{31}\text{P}$ ) NMR spectroscopy which confirmed the identity and the purity of the compounds. The presence of the transannular N→Bi interaction was

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evidenced in solution, as was also observed in solid state for compounds **89-98** which molecular structures were established by single-crystal X-ray diffraction (a selection is given in Figure 17).

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Some common features observed for these compounds in solid state are:

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- strong transannular N→Bi interactions, resulting in hypercoordinated *10-Bi-4* species, with a “see-saw” coordination geometry around the bismuth centre, the nitrogen atom being placed in *trans* to the halogen or oxygen atom, respectively. In the compounds with  group attached to nitrogen a strong intramolecular O→Bi interaction is also established, thus resulting in hypercoordinated *12-Bi-5* species.

- the heterocyclic skeleton is built from two fused similar NC<sub>3</sub>Bi rings, folded along a Bi⋯C axis, resulting in planar chirality.

- except the chlorides **94** and **97**, and the fluoride **8**, respectively, the crystals of the other compounds show the presence of dimer associations or supramolecular architectures built through interconnection of such dimers.

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(iv) The studies on the synthesis and characterization of some new palladium(II) complexes of the type [(IPr)Pd(SbAr<sub>3</sub>)Cl<sub>2</sub>] (IPr = 1,3-bis-[2,6-di(*iso*-propyl)phenyl]-imidazol-2-iliden) with homo- and heteroleptic stibanes were continued; these compounds might exhibit catalytic activity in Buchwald-Hartwig coupling reactions.

The complex  (**101**) was isolated as an orange solid with sharp melting point. It was characterized by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy, the assignment of the resonances being based on 2D spectra. This

compound was screened for catalytic activity in a Buchwald-Hartwig coupling reaction. The preliminary results suggest that a dehalogenation reaction took place instead of the expected C–N bond formation.

The molecular structure of complex **(88)**, obtained in the previous phase of the project, was established by single-crystal X-ray diffraction (Figure 18). The coordination geometry around the palladium centre is slightly distorted square-planar, with the bulky ligand in *trans* to each other.

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**Figure 18.** Molecular structure of compound

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**(88).**

### Attempts for the synthesis of new hypervalent dibismuthanes

In order to obtain diorganobismuth(III) chlorides containing the two pendant arm ligands 2,6-{MeN(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NCH<sub>2</sub>}<sub>2</sub>C<sub>6</sub>H<sub>3</sub> and 2,6-{O(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NCH<sub>2</sub>}<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, which can be used as starting materials in reduction reactions to provide the corresponding dibismuthanes (direct precursors of organometallic peroxides), attempts to prepare species of the type (R

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group of reduced volume) were carried out. For the synthesis of the compounds [R = Ph, 2-(Me<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>] either PhBiCl<sub>2</sub> or [2,6-{O(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NCH<sub>2</sub>}<sub>2</sub>C<sub>6</sub>H<sub>3</sub>]BiCl<sub>2</sub> (**55**) and [2,6-{MeN(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NCH<sub>2</sub>}<sub>2</sub>C<sub>6</sub>H<sub>3</sub>]BiCl<sub>2</sub> (**57**), prepared in previous phases of the project. It was observed an unusual remarkable inertness of compounds **55** and **57** towards a strong nucleophilic base as n-BuLi, the unchanged organobismuth(III) dichlorides being recovered from the reaction mixtures.

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For the reduction of the dichloride **57** three methods were used: (a) reduction with a Na mirror – unchanged starting material was recovered; (b) reduction with a K mirror – over-reduction to Bi(0) due to K excess (which cannot be avoided); (c) reduction with K(<sup>t</sup>Bu<sub>3</sub>BH) (as described in the literature) – an intense red compound was obtained; in addition to the formation of gaseous hydrogen, this color confirmed the reduction of the organobismuth(III) dichloride. The <sup>1</sup>H NMR of the crude red product, in C<sub>6</sub>D<sub>6</sub> under inert atmosphere, suggest the formation of several (linear or cyclic) species with various nuclearity. The reaction with O<sub>2</sub> of this product was monitored by NMR spectroscopy, but no pure compound could be isolated so far.

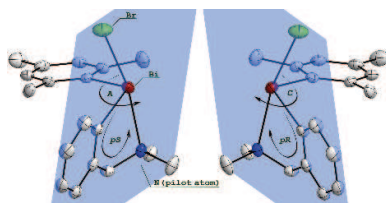
### Publications appeared in 2016



1. **Mixed triorganobismuthines RAr<sub>2</sub>Bi [Ar = C<sub>6</sub>F<sub>5</sub>, 2,4,6-(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>] and hypervalent racemic Bi-chiral diorganobismuth bromides RArBiBr (Ar = C<sub>6</sub>F<sub>5</sub>, Mes, Ph) with the ligand R = 2-(Me<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>. Influences of the organic substituent,**  
M. Olaru, M. Nema, A. Soran, H. J. Breunig and C. Silvestru,  
*Dalton Trans.*, **2016**, 45, 9419-9428.  
DOI: 10.1039/C5DT05074J

#### ABSTRACT:

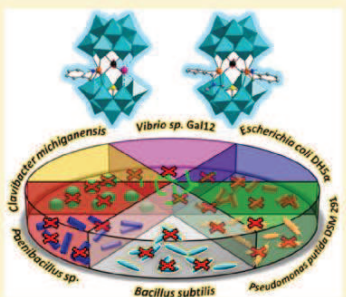
The reaction of 2-(RN=CH)C<sub>6</sub>H<sub>4</sub>MgBr [R = 2',4',6'-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub> (R<sup>1</sup>), 2',6'-i-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (R<sup>2</sup>)] [prepared from 2-(R<sup>1</sup>N=CH)C<sub>6</sub>H<sub>4</sub>Br (1) or 2-(R<sup>2</sup>N=CH)C<sub>6</sub>H<sub>4</sub>Br (2) and Mg] with SbCl<sub>3</sub> in a 2 : 1 and 1 : 1 molar ratio followed by treatment with an aqueous KBr solution gave [2-(R<sup>1</sup>N=CH)C<sub>6</sub>H<sub>4</sub>]<sub>2</sub>SbBr (3) and [2-(R<sup>2</sup>N=CH)C<sub>6</sub>H<sub>4</sub>]<sub>2</sub>SbBr (4) as well as [2-(R<sup>1</sup>N=CH)C<sub>6</sub>H<sub>4</sub>]<sub>2</sub>SbBr<sub>2</sub> (6) and [2-(R<sup>2</sup>N=CH)C<sub>6</sub>H<sub>4</sub>]<sub>2</sub>SbBr<sub>2</sub> (7). Treatment of 4 with Na<sub>2</sub>S·9H<sub>2</sub>O provided the dinuclear [{2-(R<sup>2</sup>N=CH)C<sub>6</sub>H<sub>4</sub>]<sub>2</sub>Sb]<sub>2</sub>S (5). Heterocyclic species, i.e. the oxide *cyclo*-[{2-(R<sup>2</sup>N=CH)C<sub>6</sub>H<sub>4</sub>]<sub>2</sub>SbO<sub>3</sub> (8) and the sulfides *cyclo*-[{2-(R<sup>1</sup>N=CH)C<sub>6</sub>H<sub>4</sub>]<sub>2</sub>SbS<sub>2</sub> (9) and *cyclo*-[{2-(R<sup>2</sup>N=CH)C<sub>6</sub>H<sub>4</sub>]<sub>2</sub>SbS<sub>2</sub> (10), were obtained by reacting dibromides 6 and 7 with KOH and Na<sub>2</sub>S·9H<sub>2</sub>O, respectively, in a water–toluene solvent mixture. The sulfide 10 reacted with [W(CO)<sub>5</sub>(thf)] to yield the heterometallic complex *cyclo*-[{2-(R<sup>2</sup>N=CH)C<sub>6</sub>H<sub>4</sub>]<sub>2</sub>SbS<sub>2</sub>[W(CO)<sub>5</sub>] (11). The compounds were characterised by multinuclear NMR spectroscopy in solution, mass spectrometry and IR spectroscopy in the solid state. The molecular structures of 4, 5, 6·CHCl<sub>3</sub>, 7, 9·CH<sub>2</sub>Cl<sub>2</sub>, 10 and 11·0.25CH<sub>3</sub>OH were established by single-crystal X-ray diffraction. Theoretical calculations using DFT methods were carried out on bromide 7 and the geometrical isomers of its dimer association as well as the geometrical isomers of sulfide 10 and its monomer.



2. **19-Tungstodiarсенate(III) functionalized by organoantimony(III) groups: tuning the structure-bioactivity relationship,**

P. Yang, Z. Lin, G. Alfaro-Espinoza, M. S. Ullrich, C. I. Raț, C. Silvestru and U. Kortz,  
*Inorg. Chem.*, **2016**, 55, 251-258.  
 DOI: 10.1021/acs.inorgchem.5b02189

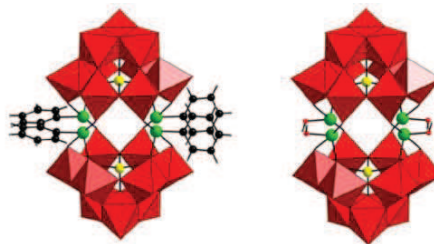
**ABSTRACT:** A family of three discrete organoantimony(III)-functionalized heteropolyanions— $[\text{Na}\{2-(\text{Me}_2\text{HN}^+\text{CH}_2)\text{C}_6\text{H}_4\text{Sb}^{\text{III}}\}_2\text{As}^{\text{III}}_2\text{W}_{19}\text{O}_{67}(\text{H}_2\text{O})\}]^{10-}$  (**1**),  $[\{2-(\text{Me}_2\text{HN}^+\text{CH}_2)\text{C}_6\text{H}_4\text{Sb}^{\text{III}}\}_2\text{As}^{\text{III}}_2\text{W}_{19}\text{O}_{67}(\text{H}_2\text{O})\}]^{8-}$  (**2**), and  $[\{2-(\text{Me}_2\text{HN}^+\text{CH}_2)\text{C}_6\text{H}_4\text{Sb}^{\text{III}}\}\{\text{WO}_2(\text{H}_2\text{O})\}\{\text{WO}(\text{H}_2\text{O})\}_2(\text{B-}\beta\text{-As}^{\text{III}}\text{W}_8\text{O}_{30})\}(\text{B-}\alpha\text{-As}^{\text{III}}\text{W}_9\text{O}_{33})_2\}]^{14-}$  (**3**)—have been prepared by one-pot reactions of the 19-tungstodiarсенate(III) precursor  $[\text{As}^{\text{III}}_2\text{W}_{19}\text{O}_{67}(\text{H}_2\text{O})]^{14-}$  with  $2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4\text{SbCl}_2$ . The three novel polyanions crystallized as the hydrated mixed-alkali salts  $\text{Cs}_3\text{KNa}_6[\text{Na}\{2-(\text{Me}_2\text{HN}^+\text{CH}_2)\text{C}_6\text{H}_4\text{Sb}^{\text{III}}\}_2\text{As}^{\text{III}}_2\text{W}_{19}\text{O}_{67}(\text{H}_2\text{O})\}]\cdot 43\text{H}_2\text{O}$  (**CsKNa-1**),  $\text{Rb}_{2.5}\text{K}_{5.5}[\{2-(\text{Me}_2\text{HN}^+\text{CH}_2)\text{C}_6\text{H}_4\text{Sb}^{\text{III}}\}_2\text{As}^{\text{III}}_2\text{W}_{19}\text{O}_{67}(\text{H}_2\text{O})\}]\cdot 18\text{H}_2\text{O}\cdot \text{Me}_2\text{NCH}_2\text{C}_6\text{H}_5$  (**RbK-2**), and  $\text{Rb}_{2.5}\text{K}_{11.5}[\{2-(\text{Me}_2\text{HN}^+\text{CH}_2)\text{C}_6\text{H}_4\text{Sb}^{\text{III}}\}\{\text{WO}_2(\text{H}_2\text{O})\}\{\text{WO}(\text{H}_2\text{O})\}_2(\text{B-}\beta\text{-As}^{\text{III}}\text{W}_8\text{O}_{30})\}(\text{B-}\alpha\text{-As}^{\text{III}}\text{W}_9\text{O}_{33})_2\}]\cdot 52\text{H}_2\text{O}$  (**RbK-3**), respectively. The number of incorporated  $\{2-(\text{Me}_2\text{HN}^+\text{CH}_2)\text{C}_6\text{H}_4\text{Sb}^{\text{III}}\}$  units could be tuned by careful control of the experimental parameters. Polyanions **1** and **2** possess a dimeric sandwich-type topology, whereas **3** features a trimeric, wheel-shaped structure, representing the largest organoantimony-containing polyanion. All three compounds were fully characterized in the solid state via single-crystal X-ray diffraction (XRD), infrared (IR) spectroscopy, and thermogravimetric analysis, and their aqueous solution stability was validated by ultraviolet–visible light (UV-vis) and multinuclear ( $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{183}\text{W}$ ) nuclear magnetic resonance (NMR) spectroscopy. Effective inhibition against six different types of bacteria was observed for **1** and **2**, and we could extract a structure–bioactivity relationship for these polyanions.



3. **Tetra-antimony(III)-bridged 18-tungsto-2-arsenates(V),  $[(\text{LSb}^{\text{III}})_4(\text{A-}\alpha\text{-As}^{\text{V}}\text{W}_9\text{O}_{34})_2]^{10-}$  (L = Ph, OH): turning bioactivity on and off by ligand substitution,**

P. Yang, Z. Lin, B. S. Bassil, G. Alfaro-Espinoza, M. S. Ullrich, M.-X. Li, C. Silvestru and U. Kortz,  
*Inorg. Chem.*, **2016**, 55, 3718-3720.  
 DOI: 10.1021/acs.inorgchem.6b00107

**ABSTRACT:** Two tetra-antimony(III)-bridged, sandwich-type 18-tungsto-2-arsenates(V),  $[(\text{LSb}^{\text{III}})_4(\text{A-}\alpha\text{-As}^{\text{V}}\text{W}_9\text{O}_{34})_2]^{10-}$  (L = Ph (**1**), OH (**2**)), were prepared and fully characterized in the solid state and in solution. Both polyanions are stable in aqueous physiological medium for at least 24 h (at concentrations  $\geq 2.5 \times 10^{-6}$  M). Despite the presence of an isostructural tetra-antimony(III) motif in **1** and **2**, distinctly different antibacterial activity was observed for both polyanions. The minimum inhibitory concentrations (MIC) of **1** (7.8–62.5  $\mu\text{g/mL}$ ) is lower than for any other organoantimony-(III)-containing polyoxometalate reported to date.



4. **Heterocyclic bismuth(III) compounds with transannular N→Bi interactions. Synthesis and structure,**  
 A. M. Toma, A. Pop, A. Silvestru, T. Rüffer, H. Lang and M. Mehring,  
**2016, to be submitted.**

**Contributions to national and international conferences**

- C1. Evaluation of the potential as catalyst for Mannich reactions of selected ionic diorganoantimony(III) compounds,  
 A. Biró, C. I. Raț and C. Silvestru  
 at *The XXXIV<sup>th</sup> Romanian Chemistry Conference*, Calimanesti-Caciulata, Valcea, October 4-7, 2016 (poster).

Director proiect,  
**Prof. Dr. Cristian Silvestru**

*Cristian Silvestru*